THE DEGRADING EFFECTS OF TRACE METALS IN THE HYDROGEN PEROXIDE BLEACHING OF COTTON

A THESIS

Presented to

the Faculty of the Graduate Division

by

Stuart David Snyder

In Partial Fulfillment

of the Requirements for the Degree

Master of Science in Textiles

Georgia Institute of Technology

September 1957

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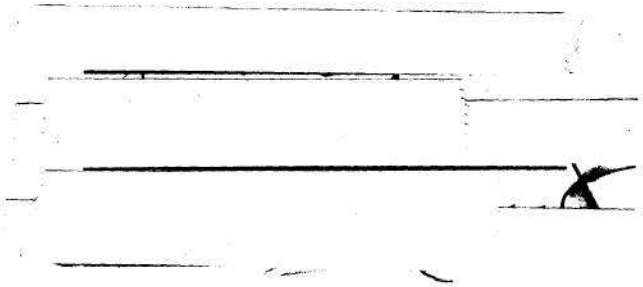

Date Approved by Chairman: Oct 3, 1956

ACKNOWLEDGEMENTS

This project could not have reached its completion without the able assistance and guidance of Dr. James L. Taylor, Professor J. Weldon McCarty, and Professor Warren E. Moeller of the Georgia Institute of Technology. My sincere appreciation is extended to these gentlemen.

I wish also to acknowledge the contribution of Dr. Paul V. Seydel of Seydel-Woolley and Company, Atlanta, Georgia. His assistance was invaluable.

My thanks are also extended to the Becco Chemical Division of the Food Machinery and Chemical Company, Buffalo, New York, for furnishing the hydrogen peroxide used in this project; to the Chemical Department of the E. I. Du Pont de Nemours and Company, Inc., Wilmington, Delaware, for the pertinent literature which it supplied; to the Chemistry Department of the Research Division of the West Point Manufacturing Company, West Point, Georgia, for the fluidity measurements which it very graciously performed; and to the Standard-Coosa-Thatcher Company, Chattanooga, Tennessee, for furnishing the cotton yarn used in this undertaking.

Last, but by no means the least important, I am grateful to those responsible for my receipt of the T. Earle Stribling Textile Memorial Fellowship, which helped make my participation in this study possible.

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THE DEGRADING EFFECTS OF TRACE METALS IN THE HYDROGEN PEROXIDE BLEACHING OF COTTON

ABSTRACT

This study grew out of the need in the textile industry for further data on the effects of heavy metals when present in trace quantities in a hydrogen peroxide bleaching system. It was the purpose of this study to determine the relative degree of cellulose degradation produced by trace quantities of iron and copper compounds acting as catalysts in the decomposition of hydrogen peroxide in bleach solutions.

The experimentation was carried out on skeins of yarn which were tested to assure similarity of breaking strengths. The only variables introduced into this project were the concentration of the contaminant, the state of the metallic contaminant, the mode of contamination, and the medium in which the contaminant was introduced. As many other variables as possible were eliminated.

The general procedure was as follows: Five gram skeins were reeled from cones of yarn. The skeins were scoured in a 4 per cent caustic soda solution at the boil for four hours. The skeins or bleach bath was contaminated with the metals, oxides, hydroxides, and salts of iron and copper. Each of these contaminating substances was utilized in molar concen-

trations of 10^{-3}, 10^{-4}, 10^{-5}, 10^{-6}, and 10^{-7} wherever possible. The metals and oxides were introduced into the system in both aqueous and oil media, while the other substances were introduced in an aqueous medium only. The skeins were then processed in the bleach bath formula for two and one-half hours at 190° F. The bleached skeins were tested for breaking strength with a Scott Model J testing machine. Fluidity measurements were made on the bleached skeins using the cupriethylene diamine hydroxide method. The results were analyzed.

Because of an excess of hydrogen peroxide in the bleaching system, there was a decided degree of damage caused by the bleach itself with no contaminants present. This gave more of an insight into the actions involved.

It was found that the presence of oil alone in the system created no tendency toward fiber degradation. The oil, when used as a carrier for the metallic contaminants, tended to subdue the effects of these contaminants produced when they had been utilized in an aqueous medium.

Of the contaminants utilized in this study, the one that showed the greatest tendency to degrade the cotton cellulose was ferrous sulfate.

Generally, it was concluded that the degree of degradation of the cotton cellulose was not necessarily increased in proportion to the concentration of the contaminating metallic substances.

It was found that the effectiveness of a metallic substance in catalyzing the decomposition of hydrogen peroxide does not necessarily indicate that it would degrade cotton cellulose in a like manner.

A secondary investigation was made using a lower peroxide concentration (1.75 per cent based on the weight of the goods). This yielded results similar to those obtained with higher peroxide concentrations.

CHAPTER I

INTRODUCTION

Great advances have been made in the technology of cotton bleaching since the early days when cotton material was stretched over grass and exposed to the sun and air in a process called "crofting." In the intervening centuries, many different methods have been devised for destroying the natural coloring matter in the cotton fiber, but none has approached the success of today's continuous hydrogen peroxide bleaching systems. They present an opportunity to use this "universal" bleaching agent so as to obtain greater economy and improved fabric characteristics. Hydrogen peroxide is considered a universal bleaching agent because of its ability to bleach not only cotton, but also wool, silk, and other textile fibers. This gives hydrogen peroxide a decided advantage over its predecessors, chlorine bleaches, for this versatility permits the bleachery to use the same equipment on various types of textile fibers. In addition, hydrogen peroxide bleaches are less vigorous in their action than chlorine bleaches; therefore, less precise control is required to prevent fiber degradation when using the peroxide bleach.[1] There are many other advantages claimed for hydrogen peroxide and, when they are reviewed, the trend toward this method of

bleaching can be readily understood.

Even in the light of today's accomplishments, however, many problems remain. One of the difficulties with which a bleacher has to contend is the possibility of fiber damage during the bleaching process. In hydrogen peroxide bleaching, there are many conditions that could cause this degradation, but among the most notorious are faulty pH control and contact with traces of heavy metals, such as iron and copper.[2] It was the purpose of this study to determine the extent of cotton fiber damage caused by the latter condition.

History.--Hydrogen peroxide (H_2O_2) was discovered in 1818 by L. J. Thenard. Its use for bleaching was suggested in 1866 by Tessie du Motay and for bleaching silk in 1878 by Lebouteaux. It was actually used as a textile bleach in 1883 by Ebell and Witz. Its use in cotton bleaching was very limited until about 1935.

The problem of fabric damage in bleaching was prevalent even before the 1930's, when hydrogen peroxide was first coming into widespread use as a bleaching agent. Bleachers of cotton goods discovered that certain metals such as iron and copper, when present in the bleaching system, exhibited a definite tendency to produce tender spots in the cloth. As a result, pains were taken to exclude all such metals from the processing equipment and from the bleach liquors. These precautions were found particularly important in peroxide bleach-

ing processes, for the decomposition of the hydrogen peroxide was discovered to be readily catalyzed by the metallic contaminants. A possible result of such excessive decomposition was the oxidation of the cotton fibers and the ultimate formation of oxycellulose.

Much experimentation has been carried out in an attempt to discover the causes and mechanisms involved in the catalyzed decomposition of the hydrogen peroxide. Although there exists an extensive body of literature dealing with the subject,[3] the greater majority is valuable today only as a descriptive guide. The reason for this is the inherent difficulty of the subject and the slowness with which an understanding of catalysis in general has developed.[4]

Iron and copper, the two metals under scrutiny in this study, have probably received the greatest amount of attention by investigators. A great quantity of literature is available dealing with the decomposition effects of pH, concentration, and temperature of the contaminated hydrogen peroxide systems. In most cases, however, the ranges and conditions that were investigated neglected the values of most interest to the modern bleacher. In addition, the experimental efforts have been directed primarily toward the effects of the catalysts on the stability of the peroxide. Studies of the degradation of bleached cellulose, caused by the catalytic decomposition of the peroxide, were grossly neglected.

Statement of the problem.--It was the purpose of this study to determine the relative degree of cellulose degradation produced by trace quantities of iron and copper compounds acting as catalysts in the decomposition of hydrogen peroxide in bleach solutions.

The variables under investigation were: (1) the concentration of the contaminant, (2) the state of the metallic contaminant, (3) the mode of contamination, and (4) the medium in which the contaminant was introduced.

Importance of the study.--A great deal of study has been projected toward an understanding of the catalytic decomposition of hydrogen peroxide, but little has been done to enlighten the textile bleacher in his quest for an explanation of fabric damage due to these factors.

It is known that under certain conditions, traces of iron and copper in a hydrogen peroxide bleach promote the degradation of the cotton cellulose. Quantitative data are not available to exhibit the actual extent of such damage. If this information were available to the textile bleacher, it would provide him with a tool to help in the understanding of this problem and more important, in its eventual removal.

Method of approach.--Since the purpose of this study was to evaluate the degrading effects on cotton of iron and copper when present in the peroxide bleach, it was necessary to eliminate as many variables as possible and concentrate on

changes of the physical and chemical states of the metals and different means of contamination. In doing so, it was also necessary to preclude the existence of other contaminating substances in the system. One step toward assurance of this condition was the exclusive use of deionized water. This was obtained by passing tap water through an ion exchange column. This resulted in the removal of solids, including silica and carbon dioxide. The purity of the water was comparable to that produced by triple distillation.[5]

Utmost care was taken to assure that no foreign contamination was introduced by the use of unclean glassware.

Another possible source of outside contamination was the purity or impurity of the chemicals used in the tests. To obviate this contamination, only the purest substances available were used. In almost every case, the chemicals were C.P. grade or purer. The majority of the compounds were reagent grade.

To assure that the bleaching operation was duplicated in every case, a bleach bath formulation was used that did not vary throughout the study as to constitution or concentrations of the constituents.

The pH was held at 11.5, which is a common value in the bleaching of cellulose.[6] The time and temperature of the bleach were held constant at two and one-half hours and 190° F, respectively.

The two metals, copper and iron, were used as contaminants in various chemical states and in various concentrations. They were introduced into the bleaching system by addition to the bleach bath and by their saturation into the yarn prior to bleaching. Their addition to the system was made from both aqueous and oil media in the cases of the metals and oxides of copper and iron, and from an aqueous medium only in the cases of the hydroxides and sulfates of these metals. The oil medium was used to simulate the presence of metal-in-oil contamination that might occur in industry if bearing grease or lubricating oil accidentally entered the bleaching system.

After bleaching, the skeins were tested for possible degradation of the cellulose. Both fluidity measurements and breaking strength tests were made. Because of the effect of oxygen on cellulose in the presence of alkali and the subsequent formation of oxycellulose, there is a proportionate loss in fiber strength. At the same time, there is a reduction in viscosity or increase in fluidity. This is closely correlated with loss in strength.[7]

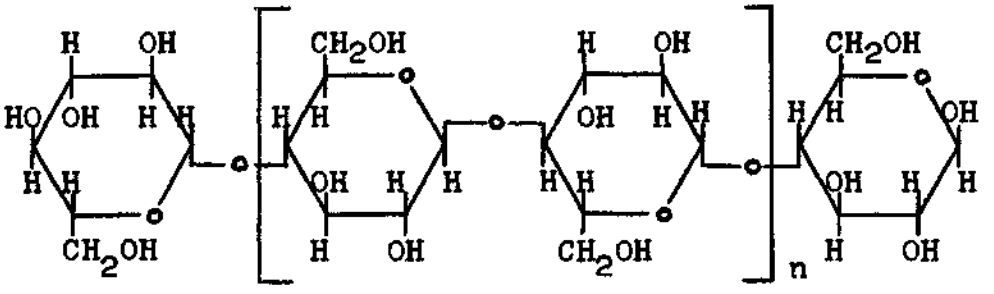
To assure that the original yarns were of the same breaking strength in all cases, each cone was tested on a Suter Single Strand Tester. The cones containing yarn of similar breaking strengths were used as a group in the reeling of skeins. No two yarns used in the bleaching were more than 0.04 pounds apart in breaking strength.

In addition to the regular formulations utilizing high concentrations of hydrogen peroxide, two lots were bleached using 1.75 per cent hydrogen peroxide (30 per cent) based on the weight of the goods. These trial bleaches were to see whether the lower concentrations of peroxide changed the behavior of the catalysts present in the system.

CHAPTER II

THEORETICAL CONSIDERATIONS

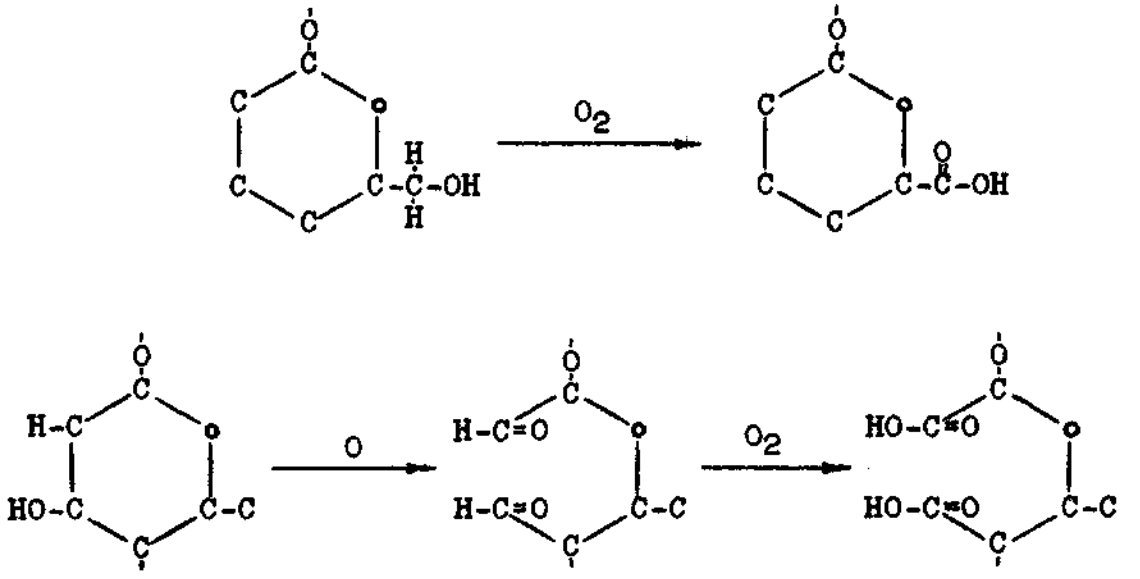
Cellulose structure.--It is the modern theory that the cellulose molecule consists of B-glucopyranose residues linked together in the 1:4 position by glucosidic oxygen bridges.[8]



This structure was first indicated by Haworth[9] in 1928, and it was subsequently established by Haworth, Hirst, and Thomas[10] that at least four contiguous B-glucopyranose units are present in the chain; however, agreement on the average chain length of the cellulose molecule has not been reached. It is believed that the average degree of polymerization of the cellulose of natural fibers is about 3000 glucose units.[11]

Oxycellulose.--This is the result of one method of chemical degradation of cellulose. It occurs when cellulose is treated with oxygen in strongly alkaline solution or with a variety of oxidizing agents over a wide range of pH. The chemical mechanisms of these reactions are not as yet completely understood.

The chemical and physical properties of the products are dependent upon the oxidizing reagent used and the acidity or basicity of the medium in which oxidation occurs. Possibilities for the primary attack are formulated as follows:



As a result of either of these types of reactions, the glucosidic bond will be weakened so that very mild reagents will attack it and cause a shortening of the average chain length. The effect of oxidation upon the degree of polymerization and upon the strength of the fiber has been investigated by many. In all cases, there is great and progressive loss of strength which may be complete as in the alkali type of cellulose, or latent, as in the periodic acid type of cellulose. In the latter, much of the strength loss becomes evident upon treatment with dilute alkalies.[12]

Oxycellulose is generally classified into two types. One is the reducing type, which is prepared in neutral or acidic solutions, and the other is the acidic type, which is formed in alkaline solutions. The acidic type of oxycellulose has sometimes been referred to as the "methylene blue type," since it exhibits a high affinity for methylene blue. Acidic oxycelluloses tend to show high alkali retention presumably due to the presence of carboxylic acid groups.[13]

Ott, Spurlin, and Grafflin[14] have developed another classification in which there are also two types. The first type contains only those materials which have the nature of a reproducible chemical individual. These oxidized celluloses are the result of the attack on specific hydroxyls in the molecule by oxidants such as periodic acid, lead tetra-acetate, and possibly nitrogen dioxide. The second type contains all other oxidized celluloses which are indefinite in structure and result from nonspecific reactions with reagents such as permanganate, chromic acid, hydrogen peroxide, and hypochlorites.

The rate of oxycellulose formation is influenced by pH, temperature, concentration of the oxidant, and the nature of the oxidizing agent itself.

The pH of the system has a considerable influence on the rate of formation of oxidized cellulose. The majority of oxidizing agents show the most rapid reaction at or near the neutral point. Clibbens and Ridge[15] have shown that at a pH

of 11.2, the rate of oxidation is considerably slower than the rate occurring at a pH of 7. Most peroxide bleaching is accomplished at or near the former value.

The rate of oxidation may also be accelerated by the presence of a third substance in the system.[16] Bartell and Cowling[17] reported that the presence of manganese or iron in alkaline cellulose greatly accelerates the rate of oxidative depolymerization while copper delays it.

The early investigators assumed that the most vulnerable spot to oxidative attack in the cellulose molecule was the primary alcohol group in position 6, which was converted to a carboxyl group. The chain degradation which accompanied this oxidation was thought to be a direct scission of the glucosidic linkages by the oxidant. Clibbens and Ridge[18] and Davidson[19] showed that the chain degradation accompanying some types of cellulose oxidation is not the result of direct scission of the molecular chain but the result of the formation of a chemically labile group which is sensitive to alkaline cleavage.

The oxidation of cellulose occurs in a heterogeneous fashion, and as a result the oxidative attack does not occur uniformly throughout the fiber but randomly.[20]

Degradation of cellulose by hydrogen peroxide.--Elöd and Vogel[21] observed that minimum degradation of cotton cellulose by hydrogen peroxide occurred around the neutral point, while

maximum degradation occurred in moderately alkaline and moderately acidic solutions. Scheller, on the other hand, observed that bleached pulp cellulose was strongly degraded by hydrogen peroxide in acidic, neutral, and strongly alkaline solution but not in moderately alkaline solution. With unbleached pulp, however, the cellulose appeared undamaged throughout the whole alkaline region but severely damaged in neutral and acid solutions. It would seem that the impurities protect the cellulose in strongly alkaline solutions.

Scheller found that after stabilizing hydrogen peroxide in a neutral solution, thereby minimizing its decomposition, the cellulose was still greatly damaged. From this observation it can be concluded that pulp cellulose is easily damaged in neutral solution regardless of the rate of decomposition of the peroxide.[22]

Decomposition of hydrogen peroxide.--Hydrogen peroxide is a relatively unstable compound. It decomposes to form oxygen and water.

$$2H_2O_2 \longrightarrow 2H_2O + O_2$$

The decomposition in the absence of catalysts is extremely slow; therefore, the solutions are stable in very pure form.

Among the factors which promote the decomposition of hydrogen peroxide are: (1) pH, (2) temperature, (3) presence of catalysts such as iron, copper, and silver, and (4) the state of these catalysts.

Nicoll and Smith[23] found that the decomposition rate was not influenced by the hydroxyl ion itself but by its reaction with impurities in the water to form catalytic hydroxides. They observed that both tap water and deionized water exhibited similar properties in that the decomposition of the hydrogen peroxide was kept to a minimum over the entire pH range studied (9.5 to 12.5). Distilled water, on the other hand, showed definite catalytic tendencies as the pH was increased. They concluded that the deionized water was almost completely devoid of heavy metal ions or other impurities that would act as catalysts; therefore, the system was relatively stable. The behavior of the tap water was explained in terms of the stabilizing tendency of the calcium and magnesium ions present in the water. These ions have long been known to be stabilizers for hydrogen peroxide and their presence in sufficient quantities in the tap water offset the activities of catalytic impurities. The behavior of the distilled water with increasing pH suggested that such water contained a strongly catalytic impurity. Spectrographic analysis revealed the presence of copper ions. These are believed to form unstable peroxides or complex per-ions with resulting decomposition of the peroxide. In addition, colloidal hydroxides are formed as the pH is increased. These exhibit an even stronger tendency to decompose the hydrogen peroxide.

The temperature of the system has a definite effect on the decomposition rate. Measurements of these rates in highly

pure, unstabilized hydrogen peroxide solutions, at temperatures varying from 50° to 70° C, have shown the rate to increase by a factor of 2.2 ± 0.1 for a 10 degree rise.[24] In bleach type solutions an increase in temperature reduces the stability of a peroxide solution, regardless of whether deionized water, C.P. chemicals, or other experimental variables are employed.[25]

Copper and iron catalyzed hydrogen peroxide decomposition.-- Copper acts both as a homogeneous and as a heterogeneous catalyst. In these respects, it is similar to iron, although less active.[26] It is common opinion that the two substances catalyze the decomposition of peroxide by much the same mechanism.[27] In the homogeneous catalysis there is an alternation between the cuprous and cupric states. The catalytic activity increases with the increase in alkalinity but does not increase regularly with an increase in concentration. At a pH of 11.6, copper sulfate exhibits a very high catalytic activity at a concentration of 10^{-7} molar and this activity passes through a minimum around a concentration of 10^{-6} molar.[28] Nicoll and Smith[29] point out that the catalytic behavior of the copper ion seems to be more likely the result of a peroxide complex than of a colloidal hydroxide, as in the case of iron. They found that copper was a more active catalyst with both sodium silicate and sodium hydroxide present in the solution than with sodium hydroxide alone. From this observation

it was concluded that the sodium silicate forms a soluble complex with copper. This complex prevents the formation of the insoluble copper hydroxide. This cupric hydroxide was found to be less active as a promoter of peroxide decomposition than ferric hydroxide. Metallic copper itself has not been observed to be particularly active, although its activity is great enough to prevent its use in equipment that might come into contact with hydrogen peroxide in some way.[30]

The iron catalyzed decomposition of hydrogen peroxide has received extensive study. Mummary[31] found that the ferrous ion, upon oxidation by hydrogen peroxide, causes the evolution of oxygen if the peroxide was present in excess. The initial liberation of oxygen occurred at a rapid rate but subsided as the ferric ion became predominant and catalysis due to it ensued. Several mechanisms have been put forth in an attempt to explain the ferrous ion oxidation. Some of these involve the formation of ferrites, FeO_4^{--}, as intermediates. Still others mention higher oxides and complexes of iron and hydrogen peroxide. In 1934, Haber and Weiss suggested a mechanism which is presently accepted.[32] This explanation assigns the hydroxyl and perhydroxyl radicals to intermediate roles. The mechanism involves the following set of reactions:

$$Fe^{++} + H_2O_2 \longrightarrow Fe^{+++} + OH + OH^- \qquad (1)$$

$$Fe^{++} + OH \longrightarrow Fe^{+++} + OH^- \qquad (2)$$

$$H_2O_2 + OH \longrightarrow O_2H + H_2O \quad (3)$$

$$Fe^{++} + O_2H \longrightarrow Fe^{+++} + O_2H^- \quad (4)$$

$$Fe^{+++} + O_2H \longrightarrow Fe^{++} + H^+ + O_2 \quad (5)$$

The catalysis of hydrogen peroxide decomposition brought about by ferric iron is explained by the reaction:

$$Fe^{+++} + O_2H \longrightarrow Fe^{++} + O_2H$$

which is followed by the reactions (1), (3), (4), and (5). The catalytic activity of ferric ions, in the pH range 10.5 - 11.4, was found to increase with alkalinity but not regularly with concentration.[33] The ferric ion acts as a stabilizer at low or moderate concentrations and as a catalyst at higher concentrations. It was observed that the maximum concentration at which the ferric ion produces a stabilizing effect is higher in the presence of sodium silicate and sodium hydroxide than in the presence of caustic soda alone. In low concentrations, peroxides or complex per-ions may be formed with iron. These are fairly stable compounds. At higher concentrations and pH values, ferric hydroxide is formed. This exhibits a powerfully catalytic action upon hydrogen peroxide decomposition. The stabilizing effect of sodium silicate may be due to its effectiveness in preventing the formation of the ferric hydroxide.

The bleaching action of hydrogen peroxide.--[34] Little is known of the nature of the chemical reactions whereby peroxides de-

stroy colored material. The action desired is that of destroying or bleaching coloring matter or converting it into a form which is soluble in water or in the bleaching agent.

The rate of bleaching by hydrogen peroxide is increased by increasing the pH of the solution. From this can be inferred that the active agent is the perhydroxyl ion, HO_2^-, which is formed by the ionization of hydrogen peroxide.

$$H_2O_2 \rightleftharpoons H^+ + HO_2^-$$

By increasing the alkalinity of the peroxide solution, the hydrogen ion concentration is decreased while at the same time, the perhydroxyl ion concentration is increased. The oxygen released by the decomposition of hydrogen peroxide has no bleaching action and may be harmful. This liberated oxygen could cause the oxidative damage in cellulose when generated in alkaline conditions, such as those prevalent in a bleach bath. Bleaching operations should be so designed as to minimize decomposition of the peroxide.

CHAPTER III

EQUIPMENT AND CHEMICALS

Beckman pH Meter, (glass electrode type), Model H-2

Illco-way Cartridge Type De-ionizer, research model

Butterworth Laboratory Type Padder

Launder-Ometer, Type LHD-EF, Style B-1

Laboratory Type, Variable Speed Electric Mixer

Analytical Balance

Scott Model J, Pendulum Type Testing Machine

Suter Single Strand Testing Machine

Suter Standard (one and one-half yards) Yarn Reel

Copper Metal Powder, purified

Iron Metal Powder, reagent

Ferrous Sulfate, reagent

Cupric Sulfate, reagent

Ferric Oxide, reagent

Cuprous Oxide, C.P.

Sodium Hydroxide, reagent

Hydrogen Peroxide, 30%, A.C.S. reagent

Sodium Meta-Silicate, reagent

Sulfuric Acid, reagent

Potassium Permanganate, C.P.

Sodium Oxalate, C.P.

Puron Engine Oil (Pure Oil Company)

Other standard laboratory equipment and materials

CHAPTER IV

EXPERIMENTAL PROCEDURE

Preparation of the Grey Yarn

Testing of Grey Yarn

The cones of yarn as received from the manufacturer were allowed to condition at 65 per cent relative humidity and 70° F for a period of not less than 48 hours. The yarn was then tested for breaking strength on a Suter Single Strand Testing Machine, the method described in A.S.T.M. Standards on Textile Materials D180-54T, section 6.[35] Twenty-five breaks were made from each cone. The cones of yarn that exhibited average breaking strengths of 0.72 ± 0.02 pounds were used in the study.

Reeling of Skeins

Five gram skeins were reeled on a Suter Standard (one and one-half yards) Yarn Reel. All metal surfaces of the reel that came into contact with the yarn were protected with gummed, cellulose tape. This prevented unwanted metallic contamination on the yarn and facilitated transfer of the skeins.

Scouring of the Grey Yarn

The five gram skeins were scoured using a 4 per cent caustic soda solution, based on the weight of the goods. A

liquor ratio of six to one was used. Deionized water was used to make up the scour liquor. The scouring was done in a two liter pyrex glass beaker. A one liter glass beaker was placed in the larger container to ensure that the skeins were kept below the liquor level. The scour was carried out in this manner at the boil for four hours. The liquor level was kept constant by the addition of deionized water during the time cycle. At the end of the prescribed time, the skeins were flood washed until all of the caustic was removed. They were then gently squeezed to remove the excess water and placed into a large beaker containing deionized water. After five minutes, the skeins were removed and again gently squeezed to remove the excess water. The yarn was then air dried.

Contamination

The metallic substances used in the contaminations were: copper metal, iron metal, cuprous oxide, ferric oxide, cupric hydroxide, ferric hydroxide, cupric sulfate, and ferrous sulfate.

The contaminating metallic compounds were introduced into the bleaching system by addition to the bleach bath or by saturation into the yarn prior to bleaching.

The iron and copper substances were utilized as contaminants in aqueous and oil media. Each of the forms of these metals were used in an aqueous medium but only the metal powders and metallic oxides were introduced in an oil medium.

Contamination of the Bleach Bath by a Metallic Substance in an Aqueous Medium

Preparation of the contaminants.--Copper metal powder was weighed on an analytical balance to obtain quantities of 0.0175, 0.0018, and 0.0002 grams of the metal. These were the quantities necessary to obtain 10^{-3}, 10^{-4}, and 10^{-5} molar concentrations, respectively, in 277 ml of the bleach bath. Each of these quantities was transferred to separate 150 ml beakers and 100 ml of deionized water was added.

Iron metal powder was prepared in much the same manner as was the copper powder, except for the quantities required. These were 0.0155, 0.0016, and 0.0002 grams, and represented eventual molar concentrations of 10^{-3}, 10^{-4}, and 10^{-5} in 277 ml of the bleach bath.

Cuprous oxide was prepared in the same manner as were the metal powders. The quantities required were 0.0424, 0.0042, and 0.0004 grams, which represented eventual molar concentrations of 10^{-3}, 10^{-4}, and 10^{-5} when entered into the bleach solution.

Ferric oxide was prepared in the same manner as were the metal powders. The quantities required were 0.044, 0.0044, and 0.0004 grams, which represented eventual molar concentrations of 10^{-3}, 10^{-4}, and 10^{-5}.

Cupric hydroxide was prepared by making a 10^{-3} molar solution of cupric sulfate. From this was extracted 27.6,

2.76, 0.28,* and 0.03 ml, each of which was placed into a separate 150 ml beaker. A second extraction of 0.28 was made and this was diluted to 27.6 ml. One more extraction of 0.28 ml was drawn from this greater volume and placed into a fifth 150 ml beaker. A 10^{-2} molar solution of sodium hydroxide was prepared. From this solution was pipetted 27.5, 2.75, 0.28, and 0.03 ml, each of which was placed into the 150 ml beakers containing respective quantities of cupric sulfate. Another extraction of 0.28 ml was made and this was diluted to 27.5 ml. Again a quantity of 0.28 ml was drawn from this larger volume and placed into the fifth 150 ml beaker.

The solutions in each of the beakers were diluted to 100 ml with deionized water. The quantities of cupric hydroxide in each of the beakers at this point represented eventual contaminant concentrations of 10^{-3}, 10^{-4}, 10^{-5}, 10^{-6}, and 10^{-7} molar in the bleach bath.

Ferric hydroxide was prepared by weighing out quantities of 0.0770 and 0.0077 grams of ferrous sulfate. These were placed in separate 150 ml beakers. A 10^{-4} molar ferrous sulfate solution was then prepared, and from this, aliquot portions of 27.7, 2.77, and 0.28 ml were extracted. Each of these quantities was placed in separate 150 ml beakers. From a 10^{-2} molar sodium hydroxide solution, quantities of 55, 5.5, 0.55, 0.06, and 0.01 ml were extracted and trans-

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*Volumes as small as this were transferred with a one milli-liter pipet graduated in one one-hundredths of a milliliter.

ferred to the beakers containing respective quantities of ferrous sulfate. These solutions were diluted to 100 ml with deionized water and then heated for 30 minutes during which time the color changed to green from the formation of Fe_3O_4 and finally brown, forming $Fe(OH)_3$.[36] The quantities of salt and alkali used were sufficient to obtain eventual hydroxide concentrations of 10^{-3}, 10^{-4}, 10^{-5}, 10^{-6}, and 10^{-7} molar in the bleach bath.

Cupric sulfate was prepared by weighing out the compound in quantities of 0.0690 and 0.0069 grams, depositing each in a 150 ml beaker, and diluting each to 100 ml with deionized water. These corresponded to 10^{-3} and 10^{-4} molar concentrations when added to the bleach bath.

To formulate the lesser concentrations, 2.75, 0.28, and 0.03 ml of a 10^{-3} molar cupric sulfate solution were transferred to 150 ml beakers and diluted to 100 ml with deionized water. They represented eventual contaminant concentrations of 10^{-5}, 10^{-6}, and 10^{-7} molar when added to the bleach bath.

Ferrous sulfate was prepared in the same general manner as was the cupric sulfate except for the quantities involved. The ferrous sulfate was weighed out in quantities of 0.077 and 0.0077 grams. From a 10^{-4} molar ferrous sulfate solution, 27.6, 2.76, and 0.28 ml were extracted and transferred to 150 ml beakers. These solutions were diluted to 100 ml as before.

The quantities represented eventual iron salt concentrations of 10^{-3}, 10^{-4}, 10^{-5}, 10^{-6}, and 10^{-7} molar when placed into the bleach bath.

Contamination of the bleach bath.--Six skeins were placed in 177 ml of the standard bleach bath contained in one liter beakers. After wetting out for five minutes, the skeins were removed as 100 ml of one of the contaminant solutions was introduced into the bleach bath. The mixture was throughly stirred with a glass rod to facilitate the diffusion of one phase in the other. The skeins were then replaced in the bath.

The yarn was bleached in the standard manner.

Contamination of the Yarn by a Metallic Substance in an Aqueous Medium

Preparation of the contaminants.--The metallic substances were prepared in precisely the same manner and in the same quantities as they had been when used in bleach bath contaminations. The only exceptions to the procedure were in the quantity of dilution and in the containers utilized.

Instead of diluting the contaminant solutions to 100 ml with deionized water, they were diluted to 277 ml.

Also, instead of using 150 ml beakers as containers for the contaminant solutions, pint glass jars of the type used in A.A.T.C.C. Launder-Ometer wash tests were utilized.

Contamination of the yarn.--Six five gram skeins were placed in each of the glass jars containing a contaminant solution. The jars were then sealed and placed on the rotor of the Launder-Ometer machine. The motor was started and the solutions were agitated by this means for 15 minutes. The temperature control on the wash testing machine was not used.

After agitation, the skeins were passed through the squeeze rolls of a laboratory-size padder. The squeeze roll pressure was adjusted so that a liquor pickup of 100 per cent was obtained on the skeins. This pressure was approximately 10 pounds.

The contaminated skeins were then immediately placed into the standard bleach bath and treated for the predetermined time interval.

Contamination of the Bleach Bath by a Metallic Substance in an Oil Medium

It was decided that three ml of the metal-bearing oil would be introduced into the bleach bath as the contaminant. This three ml contained sufficient metal (or metallic oxide) to create concentrations of those substances in the bleach bath equal to their concentrations when introduced in aqueous medium. These concentrations ranged from 10^{-3} to 10^{-5} molar. As an example, if it were desired to obtain a 10^{-3} molar copper metal concentration in 277 ml of the bleach bath, the three ml of oil would contain the necessary quantity of the

metal powder to obtain the desired concentration when added to the bleach bath.

Preparation of the contaminants.--To facilitate the handling and weighing of the small quantities, it was found desirable to weigh out $\frac{20}{3}$ of the necessary quantity of substance and mix this in 20 ml of oil. To obtain as homogeneous a mixture as possible, an electric, laboratory type of mixer was employed for 10 minutes.

Copper metal powder-quantities of 0.1167, 0.0117, and 0.0012 grams were weighed out and prepared as outlined above. These represented eventual concentrations of 10^{-3}, 10^{-4}, and 10^{-5} molar when added to the bleach bath.

Iron metal powder-quantities of 0.1033, 0.0103, and 0.0010 grams were weighed out and prepared as outlined above. These represented eventual concentrations of 10^{-3}, 10^{-4}, and 10^{-5} molar when added to the bleach bath.

Cuprous oxide-quantities of 0.2827, 0.0283, and 0.0028 grams were weighed out and prepared as outlined above. These represented eventual concentrations of 10^{-3}, 10^{-4}, and 10^{-5} molar when added to the bleach bath.

Ferric oxide-quantities of 0.2933, 0.0293, and 0.0029 grams were weighed out and prepared as outlined above. These represented concentrations of 10^{-3}, 10^{-4}, and 10^{-5} molar when added to the bleach bath.

Contamination of the bleach bath.--Immediately after mixing the metal-in-oil suspension, three ml was extracted and introduced into the bleach bath by the same method as was utilized when the contaminant had been introduced in an aqueous medium.

Bleaching was then carried on in the standard manner.

Contamination of the Yarn by a Metallic Substance in an Oil Medium

Preparation of the contaminants.--The copper metal powder and oxide, as well as the iron metal powder and oxide were prepared in the same manner and in the same concentrations as when used to contaminate the yarns from aqueous medium, with one obvious exception. Instead of using 277 ml of deionized water as the medium, the same quantity of oil was used. Also, the metal-in-oil suspension was mixed thoroughly at high speed with an electric mixer.

Contamination of the yarn.--This was carried out by the same method as was utilized in the contamination of yarn from an aqueous medium, except for the padding operation.

It was found virtually impossible to pass the skein, saturated with oil as it was, through the squeeze rolls of the laboratory-size padder. The most expedient method of padding the contaminants was found to be by drawing the skein between two adjacent fingers of one hand pressed closely together. The skein was passed through the fingers in this manner until a liquid pickup of 300 per cent was obtained.

Bleaching was carried out in the standard manner.

Bleaching

Preparation of the Bleach Bath

The bleach bath was made up containing 6 per cent sodium silicate, 1 per cent sodium hydroxide, and 7 per cent hydrogen peroxide (30 per cent).

The caustic soda was added to approximately 500 ml of deionized water in a volumetric flask, followed by the sodium silicate, and lastly the hydrogen peroxide. This was then diluted to the 1000 ml mark.

Testing of the Bleach Bath

The bleach bath was tested to determine the quantity of hydrogen peroxide in the solution and the pH of the bath.

The procedure used to determine the quantity of hydrogen peroxide in solution was the one approved by the A.A.T.C.C.[37] Briefly, it consisted of titrating an aliquot of the bleach bath with 0.588 normal potassium permanganate. The number of ml of $KMnO_4$ required, with the decimal point moved one place to the left, was the same figure as the per cent strength of the bath expressed in terms of 100 per cent hydrogen peroxide. The required quantity of hydrogen peroxide in the bleach bath was calculated to be 2.07 per cent.* If the titration revealed less than this amount, the necessary addi-

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*See appendix for derivations.

tion of hydrogen peroxide to obtain this quantity was determined by the formula:*

$$V_R = \frac{V_O\ (2.07 - P_T)}{P_T} \times 0.99$$

where

V_R = the volume of 30 per cent H_2O_2 in milliliters required in the remaining 990 ml of bleach bath, to obtain 2.07 per cent hydrogen peroxide (100 per cent) in the bath.

V_O = the volume of 30 per cent H_2O_2 in milliliters which was originally used to make up the deficient bleach bath.

P_T = the per cent of 100 per cent H_2O_2 in the bleach bath as determined by the titration.

This formula was found to give quick, easy determinations of the quantity of peroxide needed and was accurate as long as extra large quantities of peroxide were not required.

After the additional hydrogen peroxide was mixed into the bleach bath, another titration was made.

The pH measurements were made after the contaminants were introduced into the bleach solution. The measurements were made with a glass electrode pH meter. The desired pH was 11.5 and if this condition was not met, the pH was adjusted

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*See appendix for derivations.

with either sodium hydroxide or sulfuric acid, as the situation necessitated. Measurements were also made at the end of the bleach cycle.

Bleaching Procedure

A six to one liquor ratio was used (six times the liquor weight to the weight of the goods). For the six five gram skeins used in this study, this meant a volume of 177 ml of the bleach liquor. This was placed in one liter beakers. An extra 100 ml of deionized water was then added either as a contaminant carrier when the contamination was from an aqueous medium, or simply as a diluent when the contamination was from an oil medium or on the skeins.

The skeins were immersed in the bath and stirred to insure their being wet out thoroughly. Six hundred milliliter beakers were placed on top of the skeins to keep them below the liquor level.

The temperature was gradually raised to 190° F in approximately 20 minutes. The bleaching was then allowed to proceed for two and one-half hours, with stirring every 15 minutes. There was no appreciable evaporation of the bleach bath.

The skeins were removed, rinsed thoroughly, and then air dryed.

Testing of the Yarn Subsequent to Bleaching

Conditioning

The bleached skeins were conditioned in the standard atmosphere of 70° F at 65 per cent relative humidity for a period of not less than 48 hours.

Breaking Strength

The breaking strengths of the skeins were determined by the use of a Scott Model J testing machine.

The procedure used was that outlined in A.S.T.M. Tentative Method D180-54T, section 7c. The method was slightly modified in that, instead of using 120 yard skeins as prescribed by the original method, 250 yard (five gram) skeins were used.

For purposes of comparison, not only the bleached skeins were tested, but also scoured, unbleached skeins were tested.

Fluidity

The fluidity measurements were made by an outside laboratory* using the cupriethylene diamine hydroxide method. The average values of these determinations were used as sensitive measures of the degradation of the cotton fibers due to oxycellulose formation.

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*Fluidity measurements were made by the Chemical Department - Research Division of the West Point Manufacturing Company, Shawmut, Alabama.

Bleaching with Lower Concentrations of Hydrogen Peroxide

Because of the initial degradation of the yarn when using higher peroxide concentrations, a brief investigation was made to evaluate the effects of using lower peroxide concentrations.

The bleach bath was made up containing 1.75 per cent hydrogen peroxide (30 per cent), 6 per cent sodium silicate, and 0.25 per cent sodium hydroxide based on the weight of the goods.

The pH was adjusted to 11.5 with sulfuric acid and the bleaching was then carried on in the manner that was standard in this study.

The contamination was cupric sulfate and ferrous sulfate. These were introduced in the bleach bath only, and in the concentrations 10^{-3}, 10^{-4}, 10^{-5}, 10^{-6} and 10^{-7} molar.

CHAPTER V

RESULTS AND DISCUSSION OF RESULTS

Figures 1 through 6 show the breaking strengths and fluidities of skeins bleached in systems contaminated with copper substances. Figures 7 through 12 show the breaking strengths and fluidities of skeins bleached in systems contaminated with iron substances. Figures 13 and 14 show the breaking strengths and fluidities of skeins bleached in systems containing lower concentrations of hydrogen peroxide and contaminations of cupric and ferrous sulfates.

Tables 1 and 2 show the mean breaking strengths and fluidities of skeins uncontaminated by metallic substances. Tables 3 through 6 show the mean breaking strengths and fluidities of skeins bleached in systems contaminated with copper substances. Tables 7 through 10 show the mean breaking strengths and fluidities of skeins bleached in systems contaminated with iron substances. Table 11 shows the mean breaking strengths and fluidities of skeins bleached in systems containing lower concentrations of hydrogen peroxide, and cupric sulfate and ferrous sulfate contaminants.

Due to the concentration of hydrogen peroxide present in the bleach bath, there was a decided decrease in breaking strength along with an increase in the fluidity of the

bleached skeins as compared with the scoured, unbleached skeins. This degradation can be seen in Tables 1 and 2. The mean breaking strength of the scoured, unbleached skeins was 234.0 pounds and upon bleaching decreased to 83.0 pounds. The corresponding fluidities increased from 3.3 to 24.2 rhes. This initial degradation aided in the analysis of the damage brought about by catalysts, for it essentially magnified the effects and brought the differences in breaking strength down to a level that could be more easily detected.

The effects of oil in the system can also be seen in Tables 1 and 2. There seemed to be little or no difference in the breaking strengths of the skeins bleached both with and without oil present. Also, it was apparent that the oil, when present directly on the cotton fibers, made little difference in the tendency toward degradation. The corresponding fluidities showed slightly less degradation with oil present in the bath. A priori, it would be expected that the oil might decrease the surface area of the cotton fibers in contact with the bleaching solution, thereby decreasing both the bleaching action on the fibers and the liability toward oxidative damage. This, however, was not the result, probably due to the tendency of the oil to rise out of the yarn and float upon the surface of the liquor.

Figures 1 and Tables 3, 4, 5, and 6 show the effects produced by the copper metal contaminant when introduced in

Table 1. Mean Breaking Strength in Pounds of Skeins Uncontaminated by Metallic Substances

Process History of Skeins	Breaking Strength
Scoured, Unbleached	234.0
Bleached (Uncontaminated)	83.0
Bleached with Oil in Bath	84.2
Bleached with Oil on Yarn	82.8

Table 2. Fluidity in Rhes of Skeins Uncontaminated by Metallic Substances

Process History of Skeins	Breaking Strength
Scoured, Unbleached	3.3
Bleached (Uncontaminated)	24.2
Bleached with Oil in Bath	18.4
Bleached with Oil on Yarn	21.0

an aqueous medium. The copper seemed to promote the greatest degree of degradation when present in the bleach bath, but it caused considerable damage when present on the yarn at higher concentrations.

The data presented in Figure 2 and Tables 3, 4, 5, and 6 indicate a decided decrease in breaking strength when the copper metal was introduced into the system in an oil medium at relatively low concentration (10^{-5} molar). When the contaminant was introduced directly into the bleach bath there was little effect; but when the metal-bearing oil was present on the yarn, the aforementioned degradation resulted.

It can be seen in Figure 3 and Tables 3, 4, 5, and 6 that cuprous oxide in an aqueous medium, when present in the bleach bath at lower concentrations, caused little or no change in breaking strength but caused damage to the fibers at a molar concentration of 10^{-3}. When this same substance had been present on the yarn, a result was noticed that was similar to the effect of copper metal under the same conditions. In the case of the oxide, however, the effect seemed more pronounced. At the concentration of 10^{-4} molar, there appeared to be a prohibitive action toward the catalyzed degradation of the cellulose. A logical explanation may be that this phenomenon was merely the result of the rapidly catalyzed decomposition of the hydrogen peroxide, thus preventing sufficient reaction time between the liberated oxygen and the cotton cellulose. At the same time, however,

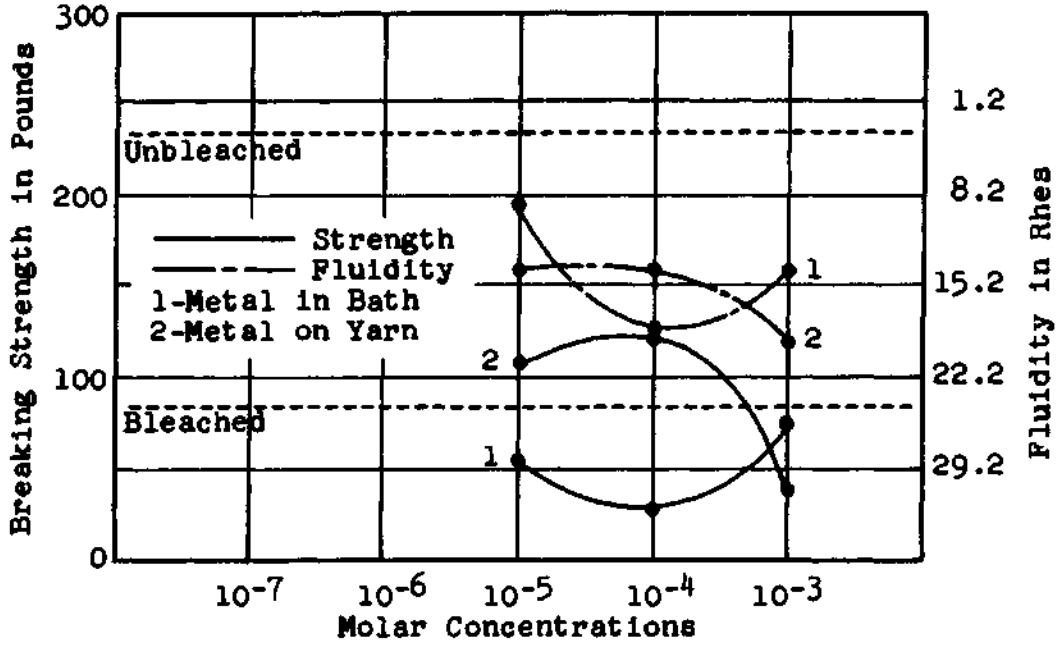

Figure 1. Breaking Strength and Fluidity of Bleached Skeins (Copper Metal Contamination from an Aqueous Medium)

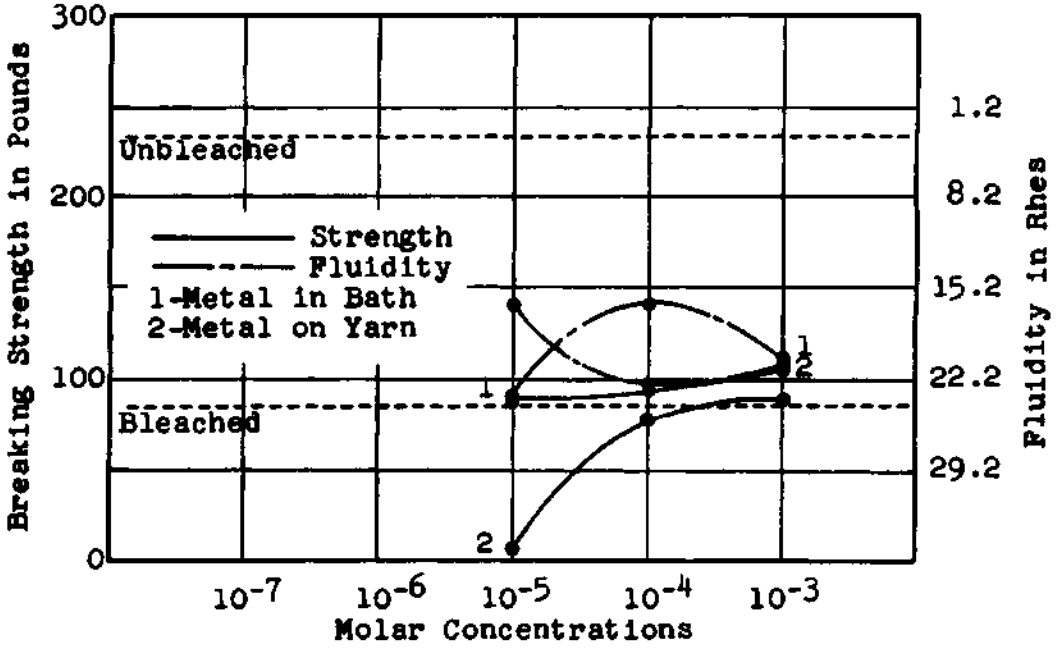

Figure 2. Breaking Strength and Fluidity of Bleached Skeins (Copper Metal Contamination from an Oil Medium)

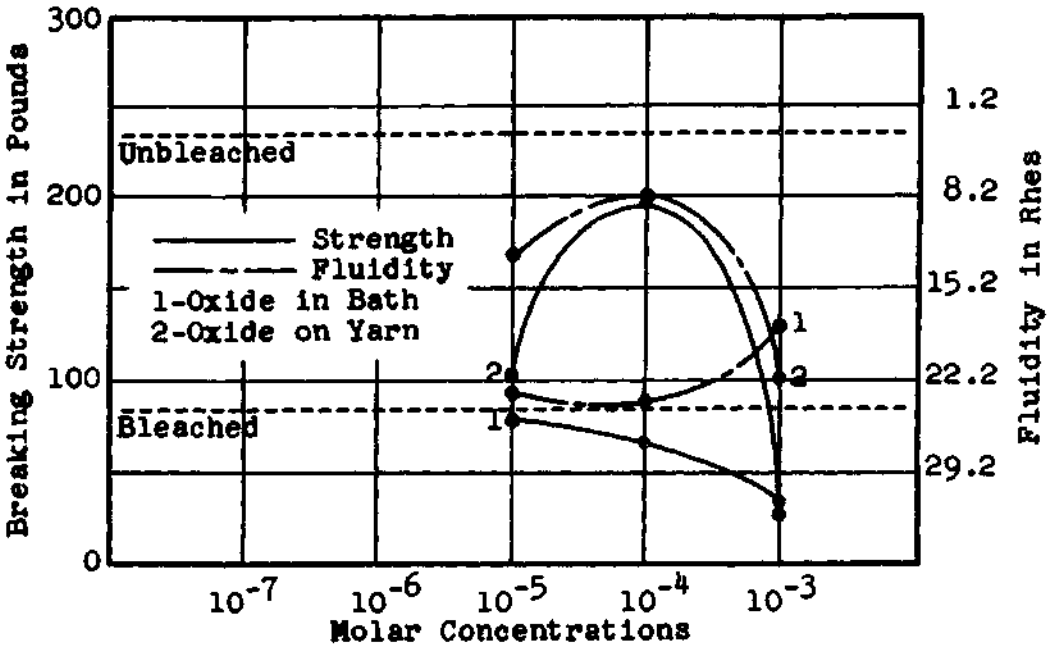

Figure 3. Breaking Strength and Fluidity of Bleached Skeins (Cuprous Oxide Contamination from an Aqueous Medium)

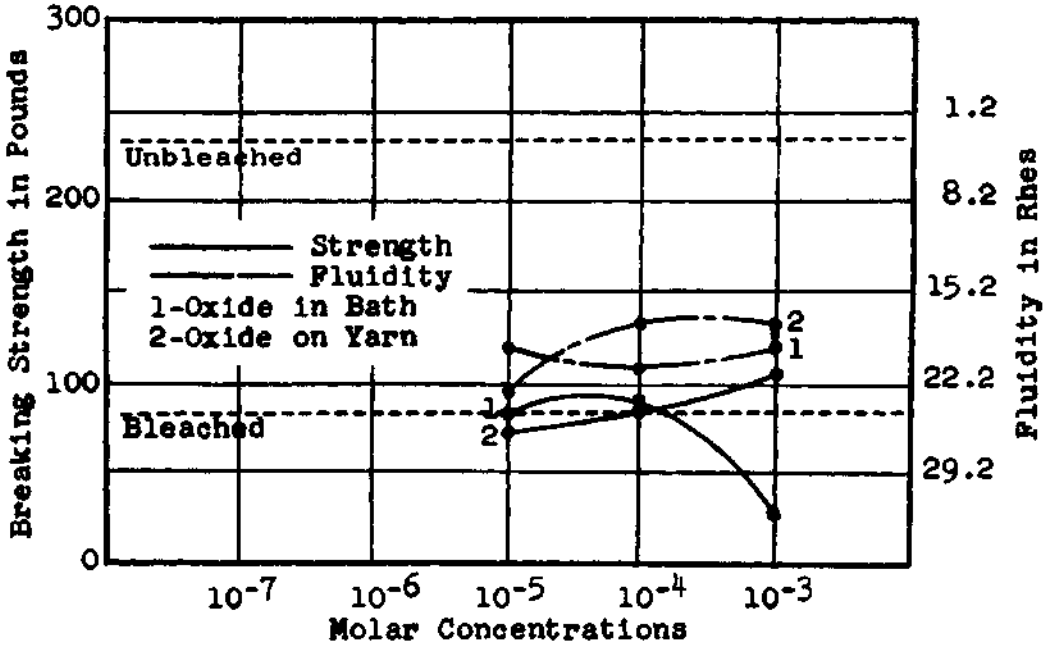

Figure 4. Breaking Strength and Fluidity of Bleached Skeins (Cuprous Oxide Contamination from an Oil Medium)

Table 3. Mean Breaking Strength in Pounds of Skeins Bleached in a Bath Contaminated with Copper

Metallic State	10^{-7}M*	10^{-6}M	10^{-5}M	10^{-4}M	10^{-3}M
Metal in Aqueous Medium	-	-	55.8	27.2	75.0
Metal in Oil Medium	-	-	92.8	91.6	105.6
Oxide in Aqueous Medium	-	-	75.4	66.2	31.0
Oxide in Oil Medium	-	-	81.6	91.2	26.6
Hydroxide in Aqueous Medium	115.2	109.4	90.0	84.8	124.0
Sulfate in Aqueous Medium	112.2	90.8	99.2	136.6	228.8

* Molar concentration

Table 4. Fluidity in Rhes of Skeins Bleached in a Bath Contaminated with Copper

Metallic State	10^{-7}M	10^{-6}M	10^{-5}M	10^{-4}M	10^{-3}M
Metal in Aqueous Medium	-	-	9.4	18.2	13.6
Metal in Oil Medium	-	-	24.0	17.0	20.1
Oxide in Aqueous Medium	-	-	23.2	24.0	18.0
Oxide in Oil Medium	-	-	19.4	20.0	19.8
Hydroxide in Aqueous Medium	15.9	17.0	16.4	17.0	11.4
Sulfate in Aqueous Medium	16.3	15.1	18.0	14.3	8.0

Table 5. Mean Breaking Strength in Pounds of Skeins Contaminated with Copper Prior to Bleaching

Metallic State	10^{-7}M	10^{-6}M	10^{-5}M	10^{-4}M	10^{-3}M
Metal in Aqueous Medium	-	-	107.3	120.0	36.4
Metal in Oil Medium	-	-	9.8	73.8	85.4
Oxide in Aqueous Medium	-	-	101.6	197.8	28.2
Oxide in Oil Medium	-	-	69.6	83.8	106.2
Hydroxide in Aqueous Medium	65.4	115.0	160.4	108.0	101.4
Sulfate in Aqueous Medium	172.8	167.6	157.0	145.2	115.2

Table 6. Fluidity in Rhes of Skeins Contaminated with Copper Prior to Bleaching

Metallic State	10^{-7}M	10^{-6}M	10^{-5}M	10^{-4}M	10^{-3}M
Metal in Aqueous Medium	-	-	13.2	13.3	19.7
Metal in Oil Medium	-	-	17.0	23.0	20.0
Oxide in Aqueous Medium	-	-	13.0	8.0	22.4
Oxide in Oil Medium	-	-	22.9	17.0	17.0
Hydroxide in Aqueous Medium	20.2	20.0	23.0	25.0	21.0
Sulfate in Aqueous Medium	14.4	18.7	16.5	12.9	16.0

there would have been little of the bleaching agent remaining in the bath and the bleaching action would have been impaired. In this study, there was no visible difference in whiteness, but it should be remembered that an excess of hydrogen peroxide was used which may have prevented decomposition of the complete bath.

The change of medium from aqueous to oil with the cuprous oxide contaminant (Figure 4 and Tables 3, 4, 5, and 6) seemed to make little difference when introduced in the bleach bath, but when present on the yarn, it seemed to subdue the effect noticed in Figure 3.

In Figure 5 and Tables 3, 4, 5, and 6, it can be seen that the presence of cupric hydroxide in the bleach bath caused slightly higher breaking strengths at both high and low concentrations. When the same substance was introduced into the system on the yarn, however, a molar concentration of 10^{-5} produced a relatively high breaking strength.

Cupric sulfate in the bleach bath at the relatively high molar concentration of 10^{-3} exhibited a sharp increase in breaking strength. This can be seen in Figure 6 and Tables 3, 4, 5, and 6. The whiteness that resulted was definitely inferior to that of the uncontaminated standard. This lack of whiteness could conceivably have been caused by a staining of the fibers due to the presence of colored hydroxides in the system. It could have also been brought about by insufficient bleaching resulting from the rapid decomposi-

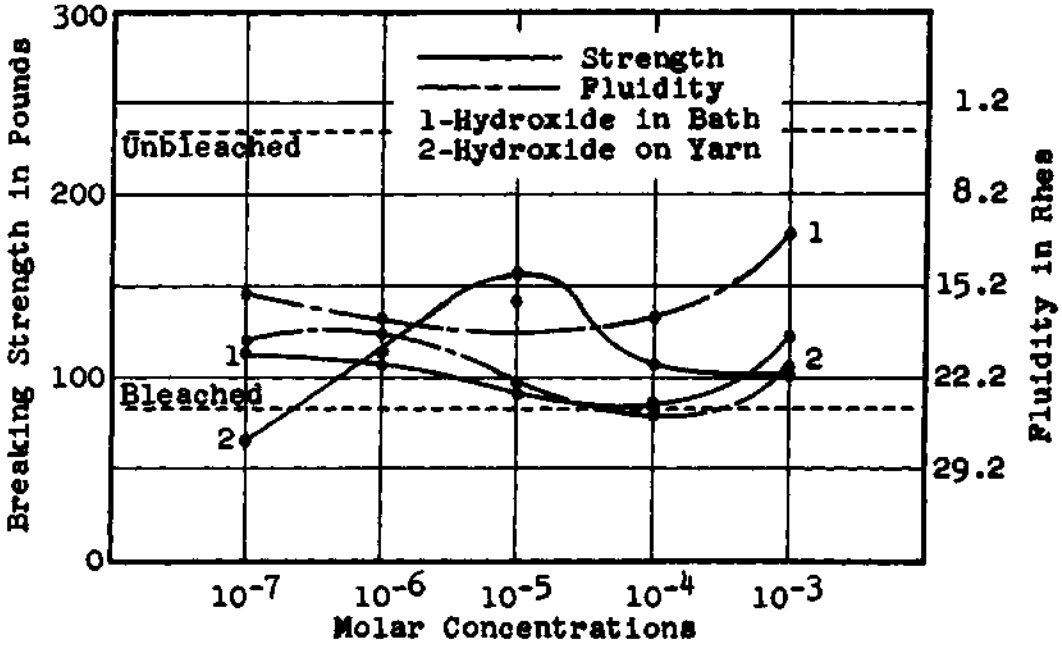

Figure 5. Breaking Strength and Fluidity of Bleached Skeins (Cupric Hydroxide Contamination from an Aqueous Medium)

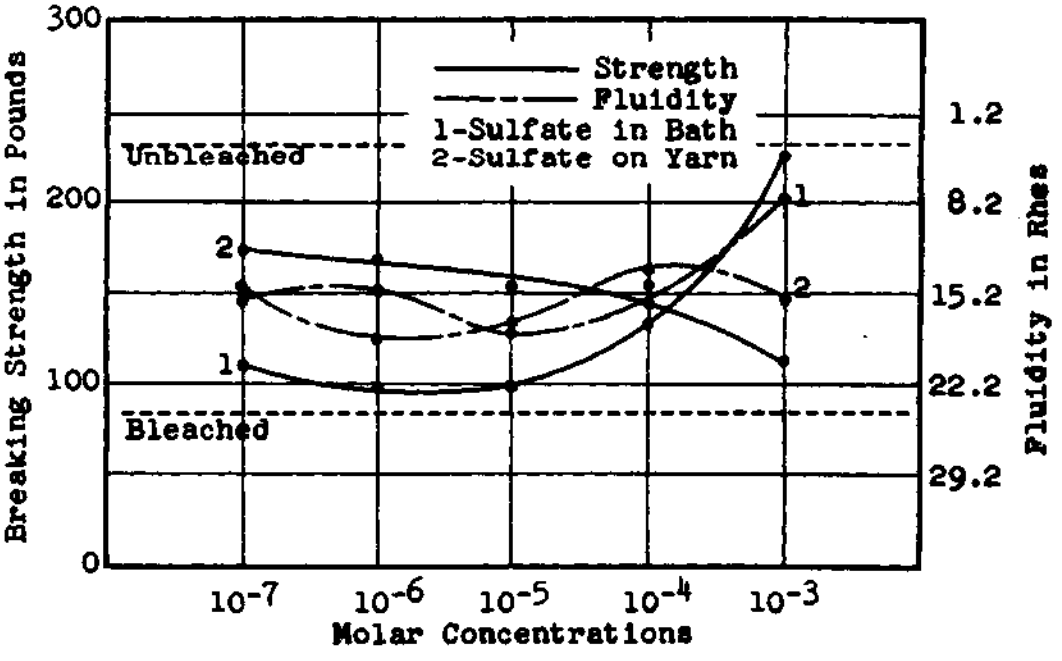

Figure 6. Breaking Strength and Fluidity of Bleached Skeins (Cupric Sulfate Contamination from an Aqueous Medium)

tion of the hydrogen peroxide in the bleach bath. This decomposition may have been catalyzed by the formation of unstable peroxides or complex per-ions and at the same time, the formation of colloidal hydroxides.[23] Also, in Figure 6 it can be seen that the copper sulfate, when present on the yarn in minute quantities (10^{-5}, 10^{-6}, and 10^{-7} molar concentrations), resulted in fairly high skein breaking strengths.

The breaking strength curves in Figure 7 show quite a different effect than that shown for copper metal under the same conditions. When the iron metal was present on the yarn there was an apparent decrease in the damage caused by the bleaching action. This may have been produced by the greater catalytic activity of iron toward the decomposition of hydrogen peroxide. If this catalyzed decomposition had proceeded at a great rate, there would not have been enough time for the generated oxygen to react with the cotton cellulose and produce its damaging effects. In this case, however, as was also observed previously with the copper metal, there was no visible difference in whiteness.

When the iron metal was introduced into the system at a molar concentration of 10^{-4} and in an oil medium (Figure 8 and Tables 7, 8, 9, and 10), an action resulted that was quite similar to that noticed with the copper metal under the same conditions.

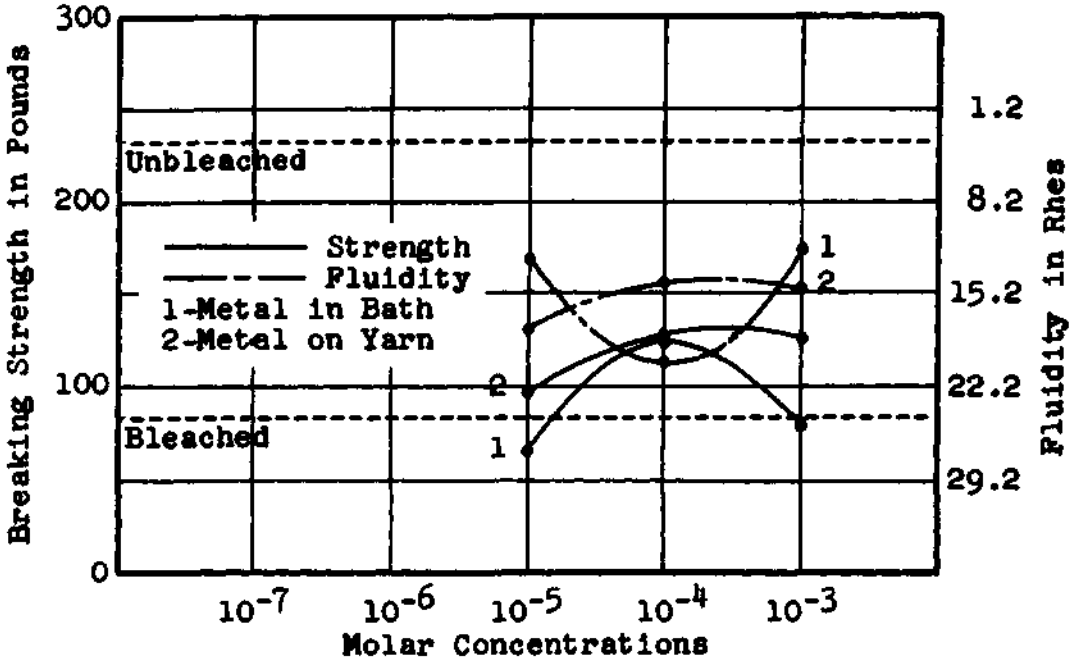

Figure 7. Breaking Strength and Fluidity of Bleached Skeins (Iron Metal Contamination from an Aqueous Medium)

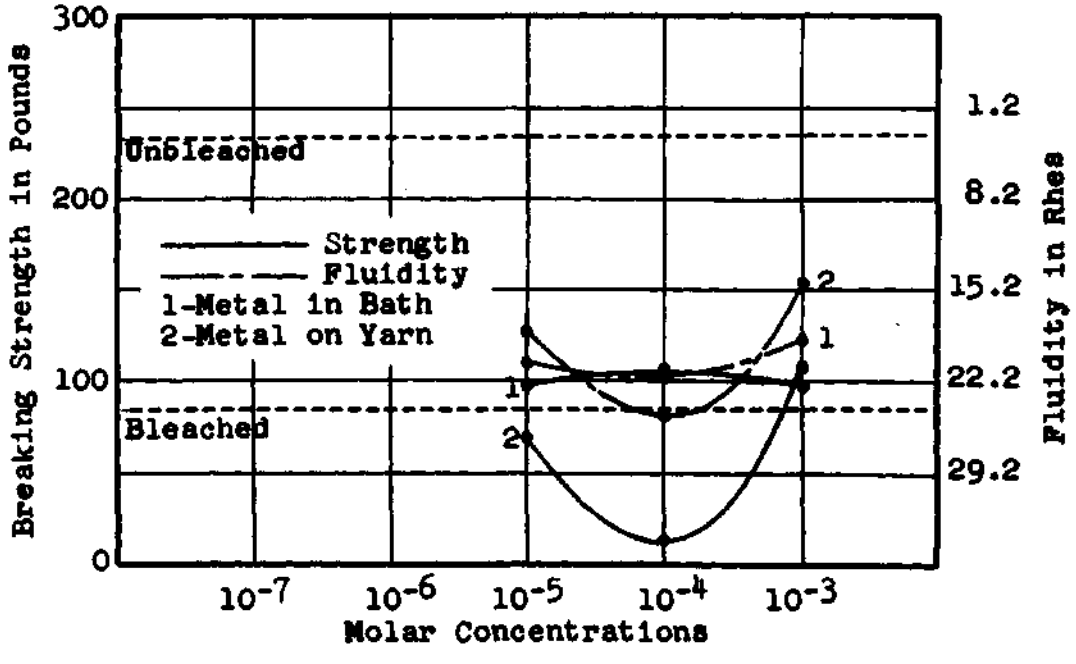

Figure 8. Breaking Strength and Fluidity of Bleached Skeins (Iron Metal Contamination from an Oil Medium)

Table 7. Mean Breaking Strength in Pounds of Skeins Bleached in a Bath Contaminated with Iron

Metallic State	10^{-7}M	10^{-6}M	10^{-5}M	10^{-4}M	10^{-3}M
Metal in Aqueous Medium	-	-	63.4	121.4	79.8
Metal in Oil Medium	-	-	98.6	107.0	98.8
Oxide in Aqueous Medium	-	-	85.0	83.8	82.4
Oxide in Oil Medium	-	-	84.0	83.0	82.4
Hydroxide in Aqueous Medium	200.0	192.4	142.0	92.2	68.4
Sulfate in Aqueous Medium	118.2	123.6	104.6	62.8	26.8

Table 8. Fluidity in Rhes of Skeins Bleached in a Bath Contaminated with Iron

Metallic State	10^{-7}M	10^{-6}M	10^{-5}M	10^{-4}M	10^{-3}M
Metal in Aqueous Medium	-	-	12.9	20.6	12.1
Metal in Oil Medium	-	-	20.0	22.1	18.3
Oxide in Aqueous Medium	-	-	21.0	22.0	24.0
Oxide in Oil Medium	-	-	13.4	21.6	26.0
Hydroxide in Aqueous Medium	12.8	16.0	13.1	21.3	22.7
Sulfate in Aqueous Medium	10.0	13.1	13.4	23.8	25.3

Table 9. Mean Breaking Strength in Pounds of Skeins Contaminated with Iron Prior to Bleaching

Metallic State	10^{-7}M	10^{-6}M	10^{-5}M	10^{-4}M	10^{-3}M
Metal in Aqueous Medium	-	-	97.8	128.7	127.2
Metal in Oil Medium	-	-	66.7	15.2	110.0
Oxide in Aqueous Medium	-	-	109.2	91.2	137.0
Oxide in Oil Medium	-	-	83.2	81.8	81.0
Hydroxide in Aqueous Medium	103.4	117.8	107.4	84.2	52.8
Sulfate in Aqueous Medium	10.2	83.4	79.6	38.4	34.2

Table 10. Fluidity in Rhes of Skeins Contaminated with Iron Prior to Bleaching

Metallic State	10^{-7}M	10^{-6}M	10^{-5}M	10^{-4}M	10^{-3}M
Metal in Aqueous Medium	-	-	17.0	14.1	14.8
Metal in Oil Medium	-	-	18.0	25.0	14.0
Oxide in Aqueous Medium	-	-	15.1	21.0	13.0
Oxide in Oil Medium	-	-	11.4	17.1	16.0
Hydroxide in Aqueous Medium	19.0	16.0	14.0	19.4	32.0
Sulfate in Aqueous Medium	26.2	26.0	24.0	27.2	34.0

The ferric oxide (Figure 9 and Tables 7, 8, 9, and 10) showed no apparent change in breaking strengths from those obtained with no contaminant present in the system except for a minor increase at the higher concentration of 10^{-3} molar when present on the yarn. A pink tinge was noticed on the skeins bleached with the heavier concentrations of the contaminant.

Figure 10 and Tables 7, 8, 9, and 10 illustrate that there was no change in breaking strengths when the ferric oxide contaminant was introduced into the bleach bath from an oil medium rather than an aqueous medium. When the metallic substance was present on the yarn, however, once again the presence of the oil seemed to subdue the phenomenon noticed when the contaminant had been introduced into the system from an aqueous medium. Evidently the oil kept the metallic contaminants entrapped within their globules and carried them to the surface of the liquor thus preventing any reaction with the cellulose or with the bleaching phase. A pink tinge was noticed in the processed skeins.

The effect of minute quantities of ferric hydroxide (Figure 11 and Tables 7, 8, 9, and 10) in the bleach bath was one of greatly increased breaking strengths which again might be attributable to the rapid breakdown of hydrogen peroxide. There seems to have been little or no effect at the higher concentrations or when the contaminating substance had been introduced on the yarn. At the higher concentration

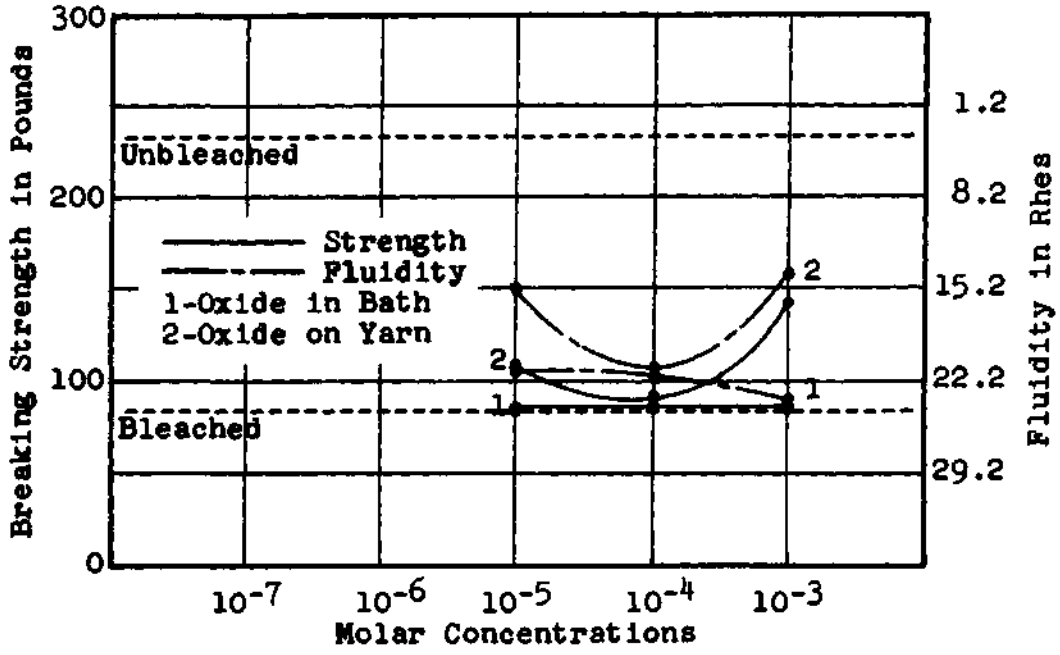

Figure 9. Breaking Strength and Fluidity of Bleached Skeins (Ferric Oxide Contamination from an Aqueous Medium)

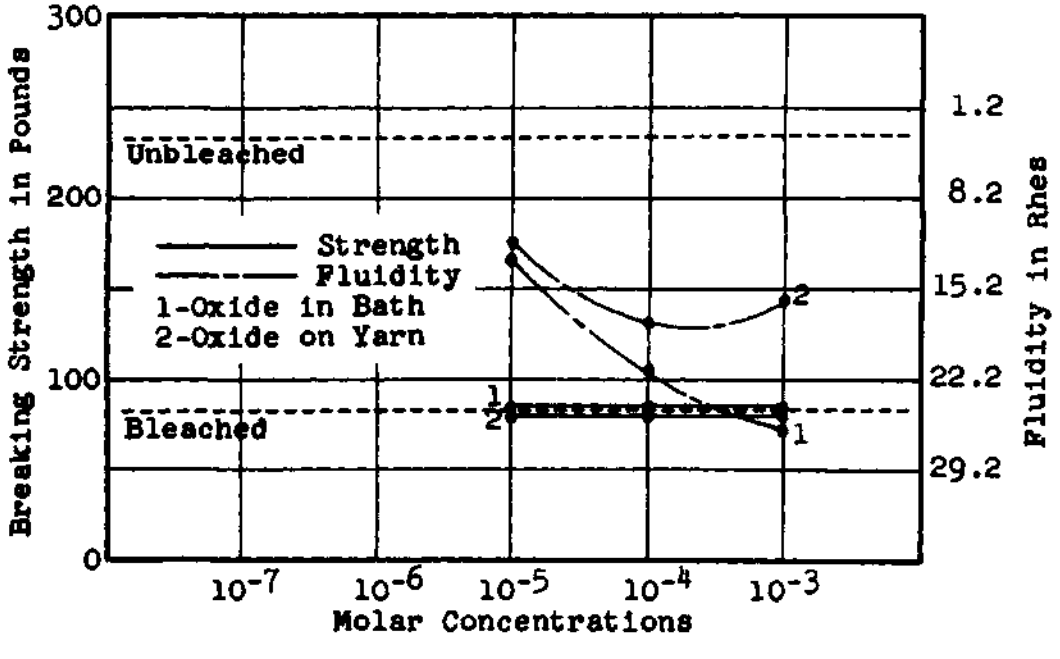

Figure 10. Breaking Strength and Fluidity of Bleached Skeins (Ferric Oxide Contamination from an Oil Medium)

of 10^{-3} molar in each case, however, the whiteness produced was not comparable to the majority of the bleached skeins. This may not have been due to the lack of bleaching action but to the staining tendency of the contaminant.

The degradation of the cotton cellulose was found to be accelerated by the presence of ferrous sulfate when in the bleach bath at high concentration and by the same substance when present on the yarn at both high and very low concentrations. This can be seen from the breaking strength curves in Figure 12 and from Tables 7, 8, 9, and 10.

Generally, the fluidities showed trends similar to those exhibited by the breaking strengths, although slightly higher. In some cases, however, the trends in fluidity seemed to be a complete reversal of those in breaking strength. Examples of this can be seen in Figures 2 and 7, and in Tables 3 through 9.

The breaking strengths were used to interpret and to reach conclusions. It was felt that this method of testing would yield results that would be more consistent and more representative of the actual fiber damage. Fluidity measurements might have been made from a section of the sample that had received little or no damage (if the sample had conceivably been damaged in a localized or random manner).

Figures 13 and 14, and Table 11 show the effects produced when the concentration of hydrogen peroxide was lowered

to 1.75 per cent (30 per cent H_2O_2) based on the weight of the goods. The trends appeared to be similar to those produced with higher peroxide concentrations. There was much closer agreement between the skein breaking strengths and the skein fluidities when the lower concentrations were used.

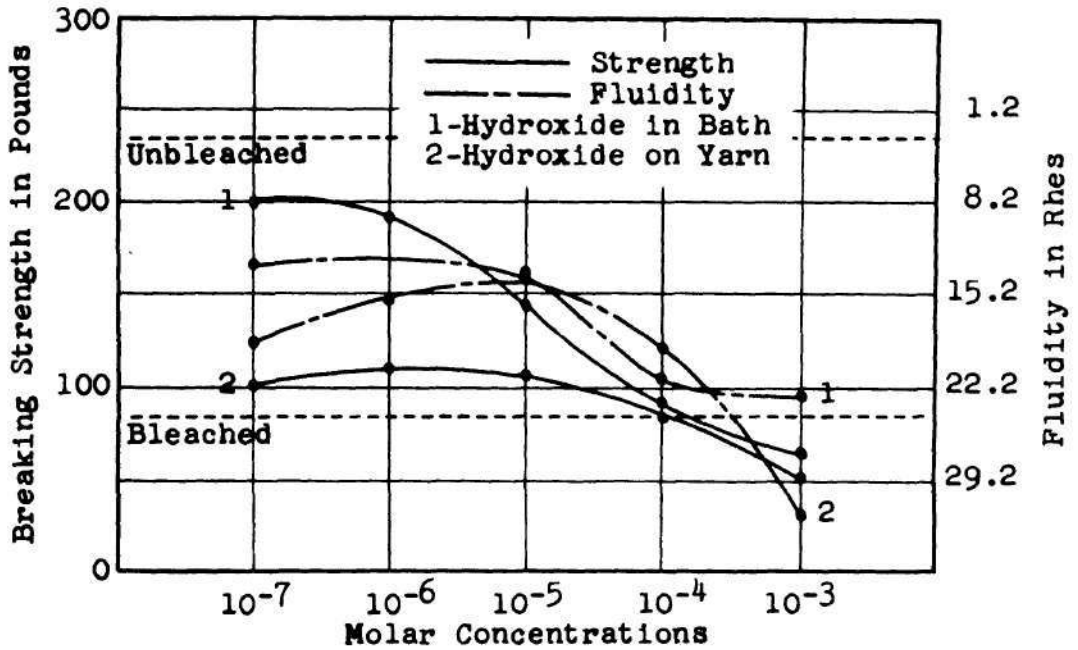

Figure 11. Breaking Strength and Fluidity of Bleached Skeins (Ferric Hydroxide Contamination from an Aqueous Medium)

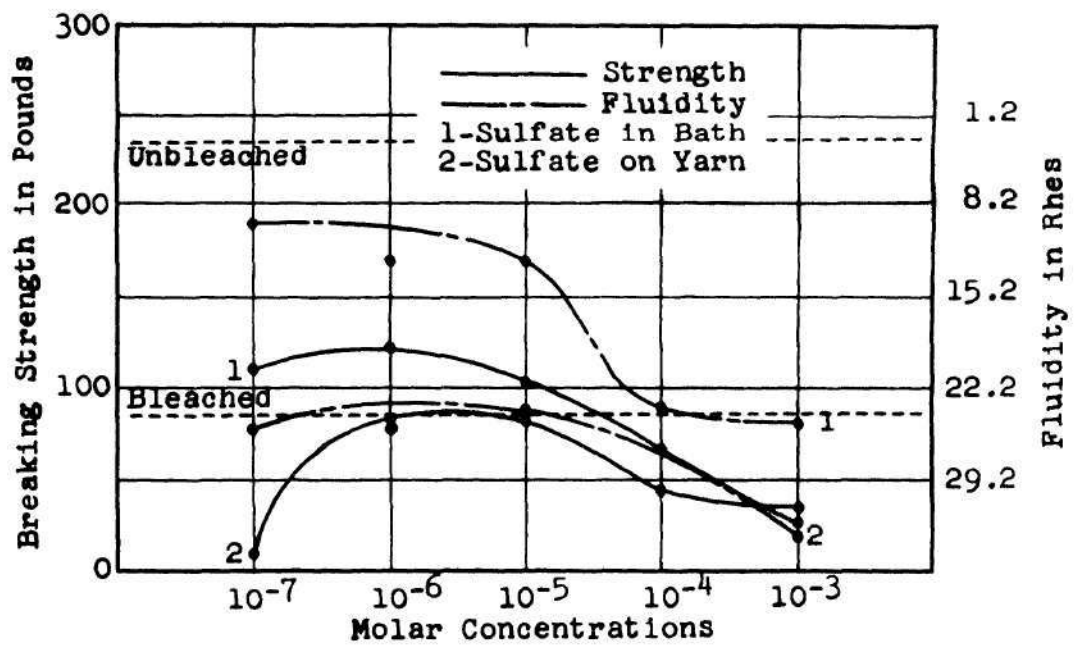

Figure 12. Breaking Strength and Fluidity of Bleached Skeins (Ferrous Sulfate Contamination from an Aqueous Medium)

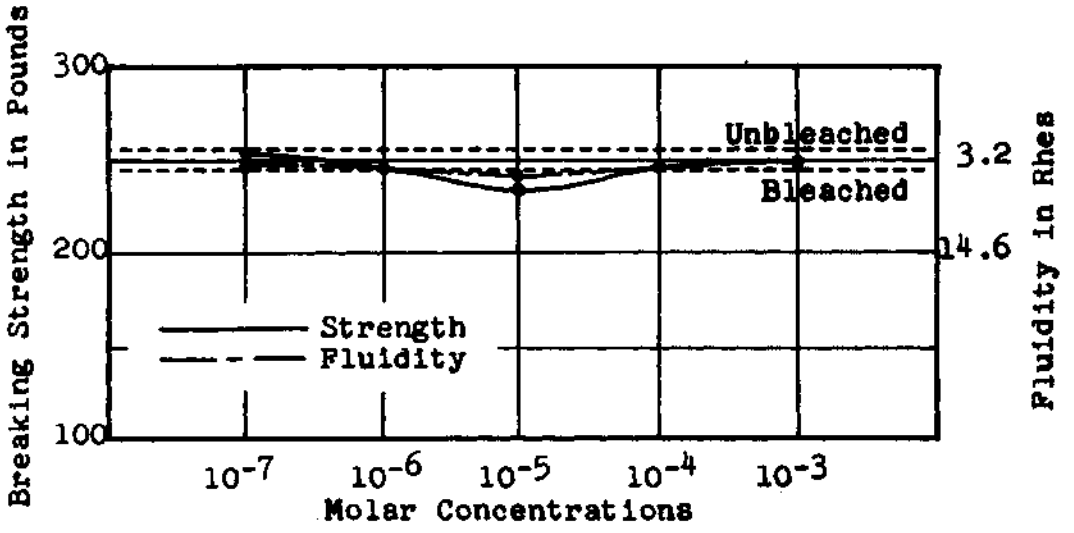

Figure 13. Breaking Strength and Fluidity of Skeins Bleached in 1.75 Per Cent Hydrogen Peroxide (Cupric Sulfate Contamination in the Bleach Bath)

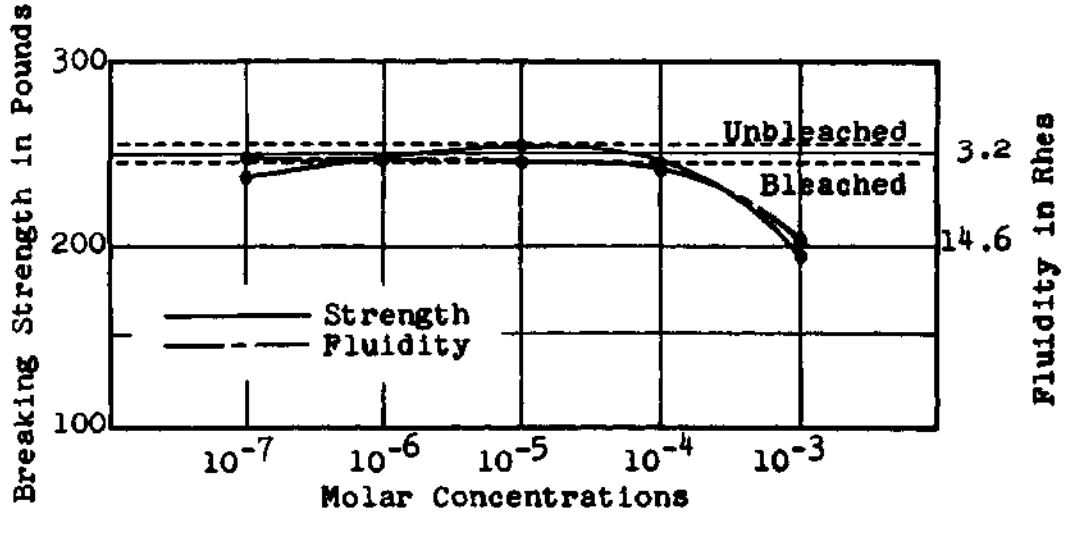

Figure 14. Breaking Strength and Fluidity of Skeins Bleached in 1.75 Per Cent Hydrogen Peroxide (Ferrous Sulfate Contamination in the Bleach Bath)

Table 11. Mean Breaking Strength in Pounds and Fluidities in Rhes of Skeins Bleached in Baths Containing Low Concentrations of Hydrogen Peroxide, and Contaminated with Cupric and Ferrous Sulfates

Molar Concentrations	Cupric Sulfate		Ferrous Sulfate	
	Strength (lbs.)	Fluidity (rhes)	Strength (lbs.)	Fluidity (rhes)
10^{-7}	252.0	3.9	238.0	3.9
10^{-6}	248.9	3.5	242.0	4.2
10^{-5}	235.2	4.4	256.0	4.7
10^{-4}	249.2	4.3	244.8	4.7
10^{-3}	249.2	3.8	194.0	12.9

The mean breaking strength of the scoured, unbleached skeins was 255.6 pounds, while that of the bleached, uncontaminated skeins was 244.4 pounds. The corresponding fluidities were 2.0 and 4.3 rhes, respectively.

CHAPTER VI

CONCLUSIONS

The conclusions that follow are based on observations that were made from the results of this study and should not be interpreted in any broader sense than that.

The presence of oil alone in the bleaching system creates no tendency toward degradation.

Copper metal exhibits a degrading tendency toward the cotton cellulose when present in the bleach bath or on the yarn in relatively large quantities or in small quantities in an oil medium.

Iron metal shows little tendency to catalyze damage in the fiber except when present on the yarn in an oil medium.

An oil medium, when used to introduce the metals of copper and iron into the bleach bath, seems to have the property of subduing the effects of these contaminants on the system.

Cuprous oxide damages the cotton fiber when present alone in the bleach bath or on the yarn, or when present on the yarn in an oil medium.

Ferric oxide exhibits little or no tendency to damage the cotton cellulose.

An oil medium, when used to contaminate yarn with the oxides of copper and iron, subdues the effects of these metallic substances on the system.

Cupric hydroxide seems to have little tendency to degrade the cotton fibers.

Ferric hydroxide causes a fairly prominent degrading effect when present in heavy concentrations.

The cupric ion, as introduced into the system in copper sulfate, shows no catalytic activity toward the degradation of the fibers.

Of the contaminants utilized in this study, the ferrous ion, as introduced into the system in ferrous sulfate, shows the greatest tendency toward fiber degradation especially when present in the system in large quantities.

The degradation of the cotton cellulose is not necessarily increased in proportion to the concentration of the contaminating metallic substances.

The effectiveness of a metallic substance to catalyze the decomposition of hydrogen peroxide does not necessarily indicate that it will degrade cotton cellulose in a like manner.

CHAPTER VII

RECOMMENDATIONS

It is recommended that further study be conducted in order to shed more light on this subject. Part of this further study should utilize a bleaching procedure that more closely parallels actual conditions. As an example, the hydrogen peroxide (30 per cent) concentration should be about 1 to 1.5 per cent based on the weight of the goods. The variables to be examined could be the same as those used in this study. To obtain a more detailed picture of the actions involved, measurements of peroxide concentrations and pH should be made at regular intervals (about every half hour) during the bleach cycle.

An investigation should be made of the catalytic activities of other metals such as nickel, tin, aluminum, manganese, and chromium. These studies could be conducted in the same manner as with the iron and copper.

The results of an unpublished study* of the degrading effects of trace metals in a caustic scour prior to hydrogen peroxide bleaching, showed that iron and copper produced latent damage in the scoured, cotton goods. The fluidities showed no great increase prior to bleaching but after the bleach the

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*Mr. Francis X. Nerney, Becco Sales Office, Charlotte, North Carolina, supplied the details concerning this study.

fluidities rose sharply. Further investigation along these lines might prove extremely beneficial.

To facilitate handling, impregnations, and testing, it is recommended that woven tapes be used in place of skeins. If, however, investigation reveals that the degrading action is highly localized, skeins should once again be employed. The breaking strength tests would not accurately show the degree of damage if the degradation were local in character.

APPENDIX

Calculation of the quantity of hydrogen peroxide desired in the bleach bath.--The quantities of hydrogen peroxide required in the bleach bath were calculated in terms of 100 per cent peroxide.

The bleach bath was made up containing 70 grams of 30 per cent hydrogen peroxide per liter. This was equivalent to 21 grams of 100 per cent hydrogen peroxide (70 x 0.30 = 21.0 grams). Ten milli-liters of bleach bath were used in the potassium permanganate titration.

$$\frac{21}{1000} = \frac{x}{10}$$

x = 0.21 grams of H_2O_2 (100 per cent) per 10 ml of bleach

Thirty grams of the bleach bath was the quantity required to obtain a six to one liquor ratio with five gram skeins. The 30 grams of bleach bath were found to occupy a volume of 29.5 ml.

$$\frac{29.5}{30} = \frac{10}{x}$$

x - 10.17 grams per 10 ml of bleach bath

$$\frac{10.17}{100} = \frac{0.21}{x}$$

x - 2.07 per cent of H_2O_2 (100 per cent) in the bleach bath

Calculation of additional hydrogen peroxide required in a deficient bleach bath.--Because of the ready decomposition of the hydrogen peroxide, it was not always at the full strength of 30 per cent. It was therefore necessary to have a means of determining the deficient quantity. The formula below is fairly accurate as long as the stock solution of hydrogen peroxide is not greatly decomposed. From the above calculation, it can be seen that 2.07 per cent of hydrogen peroxide (100 per cent) was desired in the bleach bath.

$$\frac{V_O}{P_T} = \frac{V_L}{2.07 - P_T}$$

$$V_L = \frac{V_O\ (2.07 - P_T)}{P_T}$$

where

V_L = the volume of 30 per cent hydrogen peroxide in milli-liters required per liter of bleach bath to obtain 2.07 per cent hydrogen peroxide (100 per cent) in the bath.

V_O = the volume of 30 per cent hydrogen peroxide in milli-liters that was originally used to make up the deficient bleach bath.

P_T = the per cent of hydrogen peroxide (100 per cent) in the bleach bath as determined by the titration.

Since 10 ml of bleach bath were extracted for the titration, only 990 ml remained.

$$V_R = \frac{V_O\ (2.07 - P_T)}{P_T} \times 0.99$$

where

V_R = the volume of 30 per cent hydrogen peroxide in milli-liters required in the remaining 990 ml of bleach bath to obtain 2.07 per cent hydrogen peroxide (100 per cent) in the bleach.

Table 12. Breaking Strength in Pounds of Skeins Bleached in a Bath Contaminated with Copper Metal in an Aqueous Medium

Break No.	10^{-7}M*	10^{-6}M	10^{-5}M	10^{-4}M	10^{-3}M
1	-	-	58	25	10
2	-	-	50	26	15
3	-	-	57	31	20
4	-	-	56	27	15
5	-	-	58	27	15
Totals	-	-	279	136	75
Mean	-	-	55.8	27.2	15.0
Std. Dev.	-	-	3.0	1.7	3.2
Coef. of Var.	-	-	5.4%	6.2%	21.3%

* Molar concentration

Table 13. Breaking Strength in Pounds of Bleached Skeins Contaminated with Copper Metal in an Aqueous Medium

Break No.	10^{-7}M	10^{-6}M	10^{-5}M	10^{-4}M	10^{-3}M
1	-	-	87	135	32
2	-	-	99	125	35
3	-	-	112	108	43
4	-	-	113	126	38
5	-	-	125	106	34
Totals	-	-	536	600	182
Mean	-	-	107.3	120.0	36.4
Std. Dev.	-	-	13.0	11.2	3.8
Coef. of Var.	-	-	12.1%	9.3%	11.0%

Table 14. Breaking Strength in Pounds of Skeins Bleached in a Bath Contaminated with Copper Metal in an Oil Medium

Break No.	10^{-7}M	10^{-6}M	10^{-5}M	10^{-4}M	10^{-3}M
1	-	-	90	88	100
2	-	-	90	94	107
3	-	-	99	92	109
4	-	-	87	92	107
5	-	-	98	92	105
Totals	-	-	464	458	528
Mean	-	-	92.8	91.6	105.6
Std. Dev.	-	-	4.8	2.0	3.1
Coef. of Var.	-	-	5.2%	2.2%	2.9%

Table 15. Breaking Strength in Pounds of Bleached Skeins Contaminated with Copper Metal in an Oil Medium

Break No.	10^{-7}M	10^{-6}M	10^{-5}M	10^{-4}M	10^{-3}M
1	-	-	10	76	86
2	-	-	10	70	86
3	-	-	9	71	86
4	-	-	10	71	87
5	-	-	10	81	82
Totals	-	-	49	369	427
Mean	-	-	9.8	73.8	85.4
Std. Dev.	-	-	0.4	4.2	1.8
Coef. of Var.	-	-	4.1%	5.6%	2.1%

Table 16. Breaking Strength in Pounds of Skeins Bleached in a Bath Contaminated with Cuprous Oxide in an Aqueous Medium

Break No.	10^{-7}M	10^{-6}M	10^{-5}M	10^{-4}M	10^{-3}M
1	-	-	74	69	32
2	-	-	72	67	37
3	-	-	74	68	30
4	-	-	79	67	29
5	-	-	78	60	27
Totals	-	-	377	331	155
Mean	-	-	75.4	66.2	31.0
Std. Dev.	-	-	2.7	3.2	3.4
Coef. of Var.	-	-	3.6%	4.8%	11.0%

Table 17. Breaking Strength in Pounds of Bleached Skeins Contaminated with Cuprous Oxide in an Aqueous Medium

Break No.	10^{-7}M	10^{-6}M	10^{-5}M	10^{-4}M	10^{-3}M
1	-	-	103	195	31
2	-	-	103	196	40
3	-	-	110	210	20
4	-	-	94	200	18
5	-	-	98	188	32
Totals	-	-	508	989	141
Mean	-	-	101.6	197.8	28.2
Std. Dev.	-	-	5.4	7.2	8.2
Coef. of Var.	-	-	5.3%	3.6%	28.9%

Table 18. Breaking Strength in Pounds of Skeins Bleached in a Bath Contaminated with Cuprous Oxide in an Oil Medium

Break No.	10^{-7}M	10^{-6}M	10^{-5}M	10^{-4}M	10^{-3}M
1	-	-	86	93	35
2	-	-	83	90	38
3	-	-	85	87	20
4	-	-	78	91	15
5	-	-	76	95	25
Totals	-	-	408	456	133
Mean	-	-	81.6	91.2	26.6
Std. Dev.	-	-	3.9	2.8	8.7
Coef. of Var.	-	-	4.8%	3.1%	32.7%

Table 19. Breaking Strength in Pounds of Bleached Skeins Contaminated with Cuprous Oxide in an Oil Medium

Break No.	10^{-7}M	10^{-6}M	10^{-5}M	10^{-4}M	10^{-3}M
1	-	-	77	88	113
2	-	-	63	84	112
3	-	-	67	78	100
4	-	-	72	94	90
5	-	-	69	75	116
Totals	-	-	348	419	531
Mean	-	-	69.6	83.8	106.2
Std. Dev.	-	-	4.7	6.8	9.6
Coef. of Var.	-	-	6.8%	8.1%	9.0%

Table 20. Breaking Strength in Pounds of Skeins Bleached in a Bath Contaminated with Cupric Hydroxide in an Aqueous Medium

Break No.	10^{-7}M	10^{-6}M	10^{-5}M	10^{-4}M	10^{-3}M
1	99	114	90	87	129
2	94	111	86	82	121
3	96	106	91	89	128
4	94	100	96	86	118
5	102	116	87	80	124
Totals	485	547	450	424	620
Mean	97.0	109.4	90.0	84.8	124.0
Std. Dev.	3.1	5.8	3.5	3.3	4.2
Coef. of Var.	3.2%	5.3%	3.9%	3.9%	3.4%

Table 21. Breaking Strength in Pounds of Bleached Skeins Contaminated with Cupric Hydroxide in an Aqueous Medium

Break No.	10^{-7}M	10^{-6}M	10^{-5}M	10^{-4}M	10^{-3}M
1	50	113	157	103	105
2	61	114	155	115	104
3	73	113	159	107	99
4	77	120	167	105	97
5	66	115	164	110	102
Totals	327	575	802	540	507
Mean	65.4	115.0	160.4	108.0	101.4
Std. Dev.	9.5	2.6	4.4	4.2	3.0
Coef. of Var.	14.5%	2.3%	2.8%	3.9%	3.0%

Table 22. Breaking Strength in Pounds of Skeins Bleached in a Bath Contaminated with Cupric Sulfate in an Aqueous Medium

Break No.	10^{-7}M	10^{-6}M	10^{-5}M	10^{-4}M	10^{-3}M
1	114	94	100	138	226
2	107	90	100	134	230
3	110	87	94	136	224
4	114	87	102	140	228
5	116	96	100	135	236
Totals	561	454	496	683	1144
Mean	112.2	90.8	99.2	136.6	228.8
Std. Dev.	3.2	3.6	2.7	2.2	4.1
Coef. of Var.	2.8%	4.0%	2.7%	1.6%	1.8%

Table 23. Breaking Strength in Pounds of Bleached Skeins Contaminated with Cupric Sulfate in an Aqueous Medium

Break No.	10^{-7}M	10^{-6}M	10^{-5}M	10^{-4}M	10^{-3}M
1	178	162	170	152	115
2	162	174	138	126	115
3	182	170	132	140	115
4	172	170	184	150	109
5	170	162	160	158	122
Totals	864	838	784	726	576
Mean	172.8	167.6	157.0	145.2	115.2
Std. Dev.	6.8	4.8	19.4	11.2	4.1
Coef. of Var.	3.9%	2.9%	12.3%	7.7%	3.6%

Table 24. Breaking Strength in Pounds of Skeins Bleached in a Bath Contaminated with Iron Metal in an Aqueous Medium

Break No.	10^{-7}M	10^{-6}M	10^{-5}M	10^{-4}M	10^{-3}M
1	-	-	63	121	80
2	-	-	60	121	74
3	-	-	64	120	89
4	-	-	62	125	83
5	-	-	68	120	73
Totals	-	-	317	607	399
Mean	-	-	63.4	121.4	79.8
Std. Dev.	-	-	2.8	1.9	5.9
Coef. of Var.	-	-	4.4%	1.6%	7.4%

Table 25. Breaking Strength in Pounds of Bleached Skeins Contaminated with Iron Metal in an Aqueous Medium

Break No.	10^{-7}M	10^{-6}M	10^{-5}M	10^{-4}M	10^{-3}M
1	-	-	96	124	140
2	-	-	101	135	132
3	-	-	98	129	109
4	-	-	94	125	146
5	-	-	100	130	109
Totals	-	-	489	643	636
Mean	-	-	97.8	128.7	127.2
Std. Dev.	-	-	2.6	4.0	15.5
Coef. of Var.	-	-	2.6%	3.1%	12.4%

Table 26. Breaking Strength in Pounds of Skeins Bleached in a Bath Contaminated with Iron Metal in an Oil Medium

Break No.	10^{-7}M	10^{-6}M	10^{-5}M	10^{-4}M	10^{-3}M
1	-	-	93	105	99
2	-	-	90	103	97
3	-	-	104	113	100
4	-	-	91	97	100
5	-	-	115	117	98
Totals	-	-	493	535	494
Mean	-	-	98.6	107.0	98.8
Std. Dev.	-	-	9.6	7.1	1.1
Coef. of Var.	-	-	9.7%	6.6%	1.1%

Table 27. Breaking Strength in Pounds of Bleached Skeins Contaminated with Iron Metal in an Oil Medium

Break No.	10^{-7}M	10^{-6}M	10^{-5}M	10^{-4}M	10^{-3}M
1	-	-	61	15	114
2	-	-	65	12	107
3	-	-	72	22	110
4	-	-	65	17	108
5	-	-	70	10	111
Totals	-	-	333	76	550
Mean	-	-	66.7	15.2	110.0
Std. Dev.	-	-	3.9	4.2	2.5
Coef. of Var.	-	-	5.9%	27.6%	2.2%

Table 28. Breaking Strength in Pounds of Skeins Bleached in a Bath Contaminated with Ferric Oxide in an Aqueous Medium

Break No.	10^{-7}M	10^{-6}M	10^{-5}M	10^{-4}M	10^{-3}M
1	-	-	80	77	90
2	-	-	88	94	85
3	-	-	93	76	81
4	-	-	80	90	76
5	-	-	84	82	80
Totals	-	-	425	419	412
Mean	-	-	85.0	83.8	82.4
Std. Dev.	-	-	5.0	7.1	4.8
Coef. of Var.	-	-	5.9%	8.5%	5.8%

Table 29. Breaking Strength in Pounds of Bleached Skeins Contaminated with Ferric Oxide in an Aqueous Medium

Break No.	10^{-7}M	10^{-6}M	10^{-5}M	10^{-4}M	10^{-3}M
1	-	-	113	87	139
2	-	-	104	93	134
3	-	-	110	87	136
4	-	-	112	93	138
5	-	-	107	96	138
Totals	-	-	546	456	685
Mean	-	-	109.2	91.2	137.0
Std. Dev.	-	-	3.3	3.6	1.8
Coef. of Var.	-	-	3.6%	3.9%	1.3%

Table 30. Breaking Strength in Pounds of Skeins Bleached in a Bath Contaminated with Ferric Oxide in an Oil Medium

Break No.	10^{-7}M	10^{-6}M	10^{-5}M	10^{-4}M	10^{-3}M
1	-	-	81	86	78
2	-	-	80	87	85
3	-	-	90	84	82
4	-	-	76	80	78
5	-	-	93	78	89
Totals	-	-	420	415	412
Mean	-	-	84.0	83.0	82.4
Std. Dev.	-	-	6.4	3.5	4.2
Coef. of Var.	-	-	7.6%	4.2%	5.1%

Table 31. Breaking Strength in Pounds of Bleached Skeins Contaminated with Ferric Oxide in an Oil Medium

Break No.	10^{-7}M	10^{-6}M	10^{-5}M	10^{-4}M	10^{-3}M
1	-	-	87	81	88
2	-	-	74	82	75
3	-	-	86	82	81
4	-	-	85	80	77
5	-	-	84	84	84
Totals	-	-	416	409	405
Mean	-	-	83.2	81.8	81.0
Std. Dev.	-	-	4.7	1.1	4.7
Coef. of Var.	-	-	5.6%	1.3%	5.8%

Table 32. Breaking Strength in Pounds of Skeins Bleached in a Bath Contaminated with Ferric Hydroxide in an Aqueous Medium

Break No.	10^{-7}M	10^{-6}M	10^{-5}M	10^{-4}M	10^{-3}M
1	192	186	146	92	68
2	218	198	133	96	54
3	192	186	146	91	73
4	208	204	137	94	72
5	190	188	148	88	75
Totals	1000	962	710	461	342
Mean	200.0	192.4	142.0	92.2	68.4
Std. Dev.	11.1	7.3	5.9	2.7	12.4
Coef. of Var.	5.5%	3.8%	4.2%	2.9%	18.6%

Table 33. Breaking Strength in Pounds of Bleached Skeins Contaminated with Ferric Hydroxide in an Aqueous Medium

Break No.	10^{-7}M	10^{-6}M	10^{-5}M	10^{-4}M	10^{-3}M
1	98	117	99	83	64
2	110	124	109	84	68
3	95	110	100	80	56
4	102	118	113	85	60
5	112	120	112	89	58
Totals	517	589	533	421	306
Mean	103.4	117.8	107.4	84.2	61.2
Std. Dev.	6.6	4.6	6.1	3.2	4.3
Coef. of Var.	6.4%	3.9%	5.7%	3.8%	7.1%

Table 34. Breaking Strength in Pounds of Skeins Bleached in a Bath Contaminated with Ferrous Sulfate in an Aqueous Medium

Break No.	10^{-7}M	10^{-6}M	10^{-5}M	10^{-4}M	10^{-3}M
1	100	121	99	64	28
2	122	131	113	66	24
3	113	129	97	55	23
4	124	120	113	63	27
5	132	117	101	56	32
Totals	591	618	523	314	134
Mean	118.2	123.6	104.6	62.8	26.8
Std. Dev.	10.9	5.4	7.0	4.9	3.2
Coef. of Var.	9.2%	4.4%	6.7%	7.8%	12.0%

Table 35. Breaking Strength in Pounds of Bleached Skeins Contaminated with Ferrous Sulfate in an Aqueous Medium

Break No.	10^{-7}M	10^{-6}M	10^{-5}M	10^{-4}M	10^{-3}M
1	10	85	77	40	32
2	11	80	88	45	37
3	10	82	70	32	36
4	10	83	75	42	36
5	10	87	88	33	30
Totals	51	417	398	192	171
Mean	10.2	83.4	79.6	38.4	34.2
Std. Dev.	0.3	2.4	7.2	5.1	2.6
Coef. of Var.	2.9%	2.9%	9.0%	13.6%	7.6%

Table 36. Breaking Strength in Pounds of Skeins Uncontaminated by Metallic Substances

Break No.	Scoured, Unbleached	Uncontaminated	Oil in Bath	Oil on Yarn
1	244	78	85	83
2	232	88	85	82
3	230	82	86	84
4	230	86	80	82
5	234	81	85	83
Totals	1170	415	421	414
Mean	234.0	83.0	84.2	82.8
Std. Dev.	5.2	3.6	2.1	0.95
Coef. of Var.	2.2%	4.3%	2.5%	1.1%

Table 37. Breaking Strength in Pounds of Skeins Bleached in a Bath Containing Low Concentrations of Hydrogen Peroxide and Contaminated with Cupric Sulfate

Break No.	10^{-7}M	10^{-6}M	10^{-5}M	10^{-4}M	10^{-3}M
1	250	256	244	246	248
2	244	248	234	260	246
3	266	224	226	242	250
4	242	270	232	244	262
5	258	246	240	254	240
Totals	1260	1244	1176	1246	1246
Mean	252.0	248.9	235.2	249.2	249.2
Std. Dev.	8.9	47.4	6.3	6.8	7.2
Coef. of Var.	3.5%	19.1%	2.7%	2.7%	2.9%

Table 38. Breaking Strength in Pounds of Skeins Bleached in a Bath Containing Low Concentrations of Hydrogen Peroxide and Contaminated with Ferrous Sulfate

Break No.	10^{-7}M	10^{-6}M	10^{-5}M	10^{-4}M	10^{-3}M
1	234	234	256	242	190
2	232	242	248	238	200
3	246	238	264	250	198
4	246	238	262	250	190
5	252	238	250	244	192
Totals	1210	1190	1280	1224	970
Mean	242.0	238.0	256.0	244.8	194.0
Std. Dev.	7.7	2.5	6.3	4.7	4.2
Coef. of Var.	3.2%	1.0%	2.5%	1.9%	2.2%

BIBLIOGRAPHY

1. Schumb, W. C., Satterfield, C. N., and Wentworth, R. L., Hydrogen Peroxide, American Chemical Society Monograph, No. 128, New York, Reinhold Publishing Corp., 1955, p. 576.

2. Marsh, J. T., An Introduction to Textile Bleaching, New York, John Wiley and Sons, Inc., 1948, p. 252.

3. Baxendale, J. H., Advances in Catalysis, Vol. 4, New York, Academic Press, Inc., 1952.

4. Schumb, Satterfield, and Wentworth, op. cit., p. 467.

5. Anonymous, New Cartridge Unit Deionizers, Illinois Water Treatment Co., Rockford, Illinois.

6. Nicoll, W. D. and Smith, A. F., "Stability of Dilute Alkaline Solutions of Hydrogen Peroxide," Industrial and Engineering Chemistry, 47, 1955, p. 2548.

7. Clibbens, D. A. and Ridge, B. P., "The Tensile Strength and Fluidity of Chemically Modified Cotton," Shirley Institute Memoirs, 7, 1928, p. 85.

8. Whittaker, C. M. and Wilcock, C. C., Dyeing with Coal-Tar Dyestuffs, New York, D. Van Nostrand Company, Inc., 1950, p. 57.

9. Haworth, W. N., "Structure of Cellulose and Other Polymers Related to Simple Sugars," Journal of the Society of Dyers and Colorists, 56, 1940, p.49.

10. Haworth, W. N., Hirst, E. L., and Thomas, H. A., "Polysaccarides. Part VI. Trimethyl Cellulose," Journal of the Chemical Society, 1931, p. 821.

11. Ott, E., Spurlin, H. M., and Grafflin, M. W., Cellulose and Cellulose Derivatives, Monograph on High Polymers, New York, Interscience Publishers, Inc., 1954, Vol. 5, p. 53.

12. Ward,K., Chemistry and Chemical Technology of Cotton, New York, Interscience Publishers, Inc., 1955, p. 66.

13. Birtwell, C., Clibbens, D. A., and Ridge, B. P., "Chemical Analysis of Cotton Oxycellulose, Part I.," Journal of the Textile Institute, 16, 1925, T13.

14. Ott, Spurlin, and Grafflin, op. cit., p. 145.

15. Clibbens, D. A. and Ridge, B. P., "The Chemical Analysis of Cotton-The Rate of Oxycellulose Formation," Journal of the Textile Institute, 18, 1927, T135.

16. Ott, Spurlin, and Grafflin, op. cit., p. 142.

17. Bartell, F. E. and Cowling, H., "Depolymerization of Cellulose in Viscose Production," Industrial and Engineering Chemistry, 34, 1942, p. 607.

18. Clibbens and Ridge, op. cit., T135.

19. Davidson, G. F., "The Effect of Alkalis on the Molecular Chain Length of Chemically Modified Cotton Celluloses, as Shown by Fluidity Measurements on the Derived Nitrocelluloses," Journal of the Textile Institute, 29, 1938, T195.

20. Ott, Spurlin, and Grafflin, op. cit., p. 156.

21. Ward, op. cit., p. 196.

22. Ibid., p. 198.

23. Nicoll and Smith, op. cit., p. 2549.

24. Schumb, Satterfield, and Wentworth, op. cit., p. 525.

25. Nicoll and Smith, op. cit., p. 2550.

26. Schumb, Satterfield, and Wentworth, op. cit., p. 482.

27. Baxendale, op. cit., p. 31.

28. Nicoll and Smith, op. cit., p. 2551.

29. Loc. cit.

30. Schumb, Satterfield, and Wentworth, op. cit., p. 482.

31. Mummery, C. S., "Studies on Oxidation II-The Nature of the Process in Which Hydrogen Peroxide is Utilized. Iron Salts as Catalysts," Journal of the Society of Chemical Industry, 32, 1913, p. 889.

32. Schumb, Satterfield, and Wentworth, op. cit., p. 491.

33. Nicoll and Smith, op. cit., p. 2550.

34. Schumb, Satterfield, and Wentworth, op. cit., p. 575.

35. A.S.T.M. Standards on Textile Materials, Philadelphia American Society for Testing Materials, 1956, p. 431.

36. Partington, J. R., Textbook of Inorganic Chemistry, London, MacMillan and Co., Ltd., 1950, p. 928.

37. Anonymous, "Determination of Hydrogen Peroxide in Bleach Baths," American Dyestuff Reporter, 46, 1957, p. 397.